

Draft Final Report

**Construction of a DOAS Instrument for Installation at CARB
for Low Level Measurement of SO₂ to Investigate the
Relation between SO₂ and Sulfate**

Prepared for:

**Mr. Winston Potts
Dr. John Collins**

**Research Division
California Air Resources Board
1900 14th St.
Sacramento, CA 95811
Email: wpotts@arb.ca.gov**

February 2014

Submitted by:

Dr. Thomas D. Durbin
Mr. John T. Pisano
Mr. Kurt Bumiller

University of California
CE-CERT
Riverside, CA 92521
951-781-5791
951-781-5790 (fax)

Dr. Gervase Mackay
Dr. Alak Chanda
Mr. Keith Mackay

Unisearch Associates Inc.
96 Bradwick Dr.
Concord, Ontario Canada
L4K 1K8
905-669-3547

Disclaimer

The statements and conclusions in this report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as actual or implied endorsement of such products.

Acknowledgments

This report was prepared at the University of California, Riverside, Bourns College of Engineering-Center for Environmental Research and Technology (CE-CERT). The authors thank the California Air Resources Board for funding for this study under contract No. 10-312. The authors also thank Mr. Winston Potts and Dr. John Collins for their technical and programmatic input into this study.

Table of Contents

Disclaimer	ii
Acknowledgments	ii
Table of Contents	iii
List of Figures.....	iv
List of Tables	v
Abstract.....	vi
Acronyms and Abbreviations	vii
Executive Summary	viii
Recommendations for Future Work	ix
1 Introduction	1
2 Theory of DOAS Operation.....	3
2.1 Spectroscopy	3
2.2 DOAS (Differential Optical Absorption Spectroscopy)	3
2.3 List of Pertinent Species Capable of Being Measured By DOAS	4
3 Description of DOAS Instrument.....	7
4 Test Laboratory Configuration.....	10
<i>Calibration and Gas Delivery System.....</i>	<i>10</i>
5 Performance Tests at UC Riverside.....	13
5.1 Minimum Detection Limits.....	13
5.2 Linearity Tests.....	14
5.3 Interference Tests	16
5.4 Vehicle Emission Tests	24
6 Installation/Verification at CARB Facility.....	31
7 Summary and Conclusions	32
Recommendations for Future Work	33

List of Figures

Figure 2-1 DOAS technique, in which I_0 is replaced by I'_0 , the light intensity in the absence of a structured absorption band.....	4
Figure 2-2 Absorption cross-sections of typical species measured by the DOAS technique; note SO_2 and HCHO responses which are highly important for the proposed DOAS system	5
Figure 3-1. Components of the DOAS system developed for the measurement of low level (~20 ppbV) SO_2 from vehicle exhaust	7
Figure 3-2. UV lamp and transmitter.....	8
Figure 3-3. DOAS receiver, with grating.....	8
Figure 4-1. DOAS in the Laboratory at UC Riverside	10
Figure 4-2. Overview picture of DOAS in the Laboratory at UC Riverside	10
Figure 5-1. DOAS SO_2 low dilution linearity plot	15
Figure 5-2. DOAS SO_2 high dilution linearity plot	16
Figure 5-3. Shows initial DOAS configuration file and reference spectra for SO_2	17
Figure 5-4. Shows initial DOAS configuration file and reference spectra for NO, notice strong NO absorption from 214 nm to 216 nm.....	17
Figure 5-5. Shows DOAS configuration file and reference spectra for NH_3 where the strongest absorption is.	18
Figure 5-6. Shows DOAS SO_2 , NH_3 and NO 5-second background response with only zero air flowing. Notice measured SO_2 background is slightly negative (-5 ppbv) with standard deviations between 4-5 ppbV.....	19
Figure 5-7. Shows enlarged DOAS SO_2 5-second background response with only zero air flowing. Notice measured SO_2 background again is slightly negative (-3.4ppbv) with standard deviations again between 4-5 ppbV.	19
Figure 5-8. Shows DOAS SO_2 5-second response at 80 ppbV, notice that NH_3 and NO spectra and response are unaffected by this level of SO_2	20
Figure 5-9. Shows DOAS SO_2 5-second response at 680 ppbV. Notice that NH_3 and NO spectra, as in the case of the 80 ppbV of SO_2 , have responses that are unaffected by this level of SO_2	21
Figure 5-10. Shows new DOAS configuration file and reference spectra for SO_2 with a change in spectral range of analysis to minimize NO and NH_3 interferences. The new range selected is 206-214 nm, which leaves interferences to NO of below a single standard deviation (less than 5 ppbV) of SO_2 at 300 ppmV (NO) and less than 10 ppbV of SO_2 at 16.6 ppmV (NH_3).	22
Figure 5-11. Shows DOAS SO_2 5-second background response with new fit limits to minimize NO interference NO is injected at 300 ppmV. Notice strong measured spectral lines for NO where the blue lines (measured) lay on top of the red lines (reference). The interference is below the detection limit with new fit limits.	22
Figure 5-12. Shows DOAS SO_2 5-second background response with new fit limits to minimize NH_3 as well as NO interferences. In this example 16.5 ppmV of NH_3 is injected. Notice strong measured spectral lines for NH_3 where the blue line (measured) lays on top of the red line (reference). The inteference to SO_2 at this NH_3 level is between 5-10 ppbV.....	23
Figure 5-13. Shows DOAS SO_2 5-second response at 680 ppbV using the original configuration file and spectral range of analysis between 203 and 230 nm. All linearity tests were done with this spectral range of analysis.	24

Figure 5-14. Shows DOAS SO ₂ 5-second response at 680 ppbV, using the new configuration file and spectral range of analysis between 206 and 214 nm. The response is similar at this narrower spectral range, which is where the primary SO ₂ absorptions take place.	24
Figure 5-15: Diesel test at engine turn on, note there is no detectable SO ₂ (-1.105 ppbV).....	25
Figure 5-16: progression of diesel test still SO ₂ measured below detection limit.....	25
Figure 5-17: Progression of diesel test with SO ₂ now measured above the detection limit.	26
Figure 5-18. DOAS spectral response under high NH ₃ conditions showing a negative bias to SO ₂ measured values.	27
Figure 5-19. DOAS measured values for the 2012 Nissan Versa emissions test. Note the drop off of the signal once NH ₃ levels reached 90 ppmV, and the significant negative bias to SO ₂ under these high NH ₃ conditions.	28
Figure 5-20. NH ₃ emissions measurements for the DOAS along with concurrent measurements with a tunable diode laser system configured for NH ₃ for the 2012 Nissan Versa. Both are raw exhaust measurements. Note the high similarity in response between the two separate and distinct spectral techniques.	29
Figure 5-21. Regression plot NH ₃ emissions for the 2012 Nissan Versa for the DOAS compared with an NH ₃ tunable diode laser system. Both are raw exhaust measurements. Note the high correlation between the two techniques for values up to 90 ppmV with an R ² of 0.951.....	30
Figure 5-22. DOAS Spectral response under low NH ₃ conditions, typical to diesel engines, the spectral response and the calculated numbers for SO ₂ show no negative bias.....	30

List of Tables

Table 4-1. SO ₂ test concentrations used for low dilution	11
Table 4-2. SO ₂ test concentrations used for high dilution	12
Table 5-1. SO ₂ low dilution concentration measurements.....	13
Table 5-2. SO ₂ high dilution concentration measurements	14
Table 5-3. SO ₂ low dilution concentration linearity measurements	14
Table 5-4. SO ₂ high dilution concentration linearity measurements	15

Abstract

Understanding the nature of the sulfur and sulfate in combustion and lubricant-derived particles is important to characterize to better understand the relative contribution of fuel vs. oil sulfur, to understand storage vs release of sulfur from catalyzed surfaces, and measure the sulfur fraction partitioning into the PM nucleation particles. The objective of this research is to construct, test and provide to ARB laboratories a differential optical absorption spectrometer (DOAS) that can measure down to 20 ppbV in real time and determine a mass balance between SO₂ and sulfate. The DOAS developed under this program was evaluated using a series of laboratory performance tests at the CE-CERT laboratory. The DOAS will be installed and operated in the ARB Heavy Duty Emissions Test Laboratory.

The differential optical absorption spectrometer (DOAS) developed for this project was specially designed and built for rapid, extractive detection of sulfur dioxide at low ppb levels for the ARB. The integrated system consists of the extractive sampling train, the sampling cell, and the spectrometer. The sample cell uses a single-path design with beam expanding and focusing optics to minimize cell volume. The sample cell for the UC Riverside system is cylindrical with a length of 1.0 m and a total volume of approximately 0.51 liters. To avoid possible interferences from other exhaust constituents, the spectral range was restricted to the UVB region (200–230 nanometer (nm)). A deuterium lamp was used as the light source. The cell is designed to operate over a full 8-10 hour testing day at a temperature of 110°C, with a temperature range from 25°C up to 120°C (250°F).

Laboratory tests were conducted to evaluate the response of the SO₂ monitor to a range of operating conditions, from ambient conditions to those most representative of exhaust gas emanating from vehicles. These laboratory tests showed detection limits were approximately in the range of 12 to 15 ppbV. The instrument showed good linearity over SO₂ concentration ranges of 20 to 953 ppbV. A number of interference tests were conducted, focusing on potential interferences between SO₂, NO, and NH₃. Initial tests showed some interference with either NO or NH₃, at levels of 80 ppbV and 680 ppbV. Initial tests at 300 ppmV of NO and 16.6 ppmV of NH₃ confirmed that at these high levels they would interfere with the SO₂ response over the spectral range specified. With a modification of the spectral range to 206 to 214 nm, the DOAS interference SO₂ response was less than 1.5 ppbV with 300 ppmV of NO injected with, and was slight less than 8 ppbV with 16.6 ppmV of NH₃ injected.

The DOAS was evaluated over vehicle emissions tests in CE-CERT's light-duty chassis dynamometer laboratory. The results showed no appreciable SO₂ interferences for the tests on the diesel truck, which had very low NH₃ emissions. Clearly, in a low NH₃ environment, as tested here the SO₂ detection is unbiased and meets the laboratory tested detection limits of around 20 ppbV. If the DOAS is used in a low NH₃ environment, as in this test, it should achieve the expected detection limits. The gasoline vehicles, on the other, had higher levels of NH₃, and showed a significant interference, especially when the NH₃ values exceeded 11 ppmV. If it is to be used for vehicles with higher levels of NH₃, an NH₃ scrubber would likely be needed to scrub the level of NH₃ in the exhaust to no greater than 10 ppmV, as well as perhaps some additional updates to the software that are currently being developed.

Acronyms and Abbreviations

ARB	Air Resources Board
CARB.....	California Air Resources Board
CE-CERT.....	College of Engineering-Center for Environmental Research and Technology (University of California, Riverside)
CFO.....	critical flow orifice
CCD	charge-coupled device
CPU.....	central processor unit
DECSE.....	Diesel Emission Control – Sulfur Effects project
DOAS.....	differential optical absorption spectroscopy
DPF	diesel particulate filter
mm	millimeter
NIST.....	National Institute of Standards and Technology
nm	nanometer
NO _x	nitrogen oxides
PM.....	Particulate matter
SCR.....	selective catalytic reduction
SO ₂	sulfur dioxide
SSR	solid-state relays
UCR	University of California at Riverside
UV.....	ultraviolet

Executive Summary

Since sulfur and sulfate are some of the main components of combustion and lubricant-derived particles, it is important to characterize sulfur species to understand the composition and potential health impacts of particles. Sulfate levels in vehicle exhaust particulates can be readily measured, but it is important to understand the relative contribution between combustion and oil-derived particles and the conversion rates found for SO₂ to sulfate. With the low level of sulfur present in the fuel and oil products used in modern vehicles, detection limits in the ppb range are needed to measure the SO₂ contribution.

One technique that has been shown to provide real-time, low-level measurement of engine-out SO₂, is differential optical absorption spectroscopy (DOAS). DOAS technology provides the potential for very low detection limits, along with the capability of measuring SO₂ in real-time. Over the past decade, there have been numerous advances in DOAS technology that have allowed for the development of instruments with lower detection limits in conjunction with smaller sample cells to provide improved residence times. The objective of this study was to construct, test, and provide the ARB with a state-of-the-art DOAS that can measure SO₂ down to 20 ppbV in real-time. The DOAS developed under this program was evaluated using a series of laboratory performance tests at the CE-CERT laboratory. The DOAS will be installed and operated in the ARB Heavy Duty Emissions Test Laboratory. The major conclusions from the findings are summarized in the following:

- The differential optical absorption spectrometer (DOAS) developed for this project was specially designed and built for rapid, extractive detection of sulfur dioxide at low ppb levels for the ARB. The integrated system consists of the extractive sampling train, the sampling cell, and the spectrometer.
- The sample cell uses a single-path design with beam expanding and focusing optics to minimize cell volume. The sample cell designed as an open cell with the sample cell residing between the windows, rather than having the transmitting and collecting optics inside the sample cell.
- The sample cell for this system is cylindrical with a length of 1.0 m. The total volume of the DOAS sample cell is approximately 0.51 liters.
- The cell is designed to operate over a full 8-10 hour testing day at a temperature of 110°C, with a temperature range from 25°C up to 120°C (250°F).
- To avoid possible interferences from other exhaust constituents, the spectral range was restricted to the UVB region (200–230 nanometer (nm)). For the 200–230 nanometer (nm) region, a deuterium lamp was used as the light source. Some additional adjustments were also made to the DOAS to narrow the spectral range to 206 nm to 214 nm, to compensate for an NH₃ interferent.
- The spectrometer/receiver consists of a single working element, a concave 1200 groove/millimeter (mm) holographic diffraction grating optimized for 200–230 nm.
- The DOAS software, LasIRView 2009, is a user-friendly Windows-based based package with outputs for data logging and a software manual.
- Laboratory tests were conducted to evaluate the response of the SO₂ monitor to a range of operating conditions, from ambient conditions to those most representative of exhaust gas emanating from vehicles.
- Detection limits were approximately in the range of 12 to 15 ppbV at three times the standard deviation of zero gas response.

- The linearity of the instrument was evaluated over SO₂ concentration ranges of 20 to 192 ppbV and 51 to 953 ppbV. The regression analysis showed a slope of 1.011 and 0.995, respectively, and R² values of 1.0 and 0.999, respectively, for these ranges.
- A number of interference tests were conducted, focusing on potential interferences between SO₂, NO, and NH₃. SO₂ was not found to interfere with either NO or NH₃, at levels of 80 ppbV and 680 ppbV. Initial tests at 300 ppmV of NO and 16.6 ppmV of NH₃ confirmed that at these high levels they would interfere with the SO₂ response over the spectral range specified. To mitigate the impact of these interferences, the spectral range was modified to focus on a narrower range of 206 to 214 nm. With the new spectral range of analysis, the DOAS interference SO₂ response was less than 1.5 ppbV with 300 ppmV of NO injected with, and was slight less than 8 ppbV with 16.6 ppmV of NH₃ injected.
- The DOAS was evaluated over vehicle emissions tests in CE-CERT's light-duty chassis dynamometer laboratory. A 2012 Nissan Versa, a 2013 VW Jetta GLI, and a 2013 Dodge Ram 2500 diesel pickup truck were tested. The results showed no appreciable SO₂ interferences for the tests on the diesel truck, which had very low NH₃ emissions. Clearly, in a low NH₃ environment, as tested here the SO₂ detection is unbiased and meets the laboratory tested detection limits of around 20 ppbV. If the DOAS is used in a low NH₃ environment, as in this test, it should achieve the expected detection limits.
- The gasoline vehicles, on the other, had higher levels of NH₃, and showed a significant interference. Essentially, when the NH₃ values exceeded 11 ppmV, the SO₂ measured values go negative. This interference is also non-linear as once the NH₃ values approach 80 ppmV, the SO₂ measured values are greater than -900 ppbV. If it is to be used for vehicles with higher levels of NH₃, an NH₃ scrubber would likely be needed to scrub the level of NH₃ in the exhaust to no greater than 10 ppmV, as well as perhaps some additional updates to the software that are currently being developed.
- This DOAS also has the capability of measuring NH₃ in real-time. Comparisons were made between the DOAS and an NH₃ tunable diode laser. The results showed a good correlation between the TDL and DOAS results for NH₃, at NH₃ levels below 90 ppmV, with a regression coefficient of R² = .951, but once the NH₃ levels exceed 90 ppmV the DOAS UV light source is too attenuated to make a measurement.

Recommendations for Future Work

Based on the results of this study, several recommendations for future work can be provided. This includes recommendations for further development of the instrument, as well as recommendations based on the laboratory testing that was conducted. For the DOAS itself, the initial work report here suggests that this instrument could be further developed/optimized to provide concurrent measurements of NO and NH₃. To expand the measurement capability for the NH₃, some additional development work would be needed to address the fact that the DOAS UV light source is too attenuated to make a measurement once the NH₃ levels exceed 90 ppm. The possibility of expanding the DOAS for use in other applications or for other species is also potentially of value. Another interesting finding from the laboratory tests was the higher than expected NH₃ emissions for some of the test vehicles. In particular, both of the gasoline vehicles tested for this study produced higher than expected NH₃ emissions, even though both vehicles represented late model vehicle technologies. While these vehicles were tested under a very narrow range of conditions, these initial results suggest that further investigation over a wider range of vehicles and conditions to see how prevalent the higher NH₃ emissions levels might be and if this could be an important issue with respect to tailpipe emissions.

1 Introduction

Improving air quality and meeting increasingly more stringent ambient air standards is an important factor in improving human health and overall quality of life. Emissions from vehicles and internal combustion engines have long been one of the most important contributors to the emissions inventory. Governmental regulations have targeted the reduction of emissions from such sources for a number of decades now, with advances in aftertreatment systems being a critical factor in the continuing reduction of the emission level standards. For gasoline vehicles, catalysts have been an integral part of their emissions control systems since the mid-1970s. More recently, aftertreatment systems have also been implemented for diesel engines, with the most recent regulations for diesel engines in 2007 and 2010 requiring significant reductions in particulate matter (PM) and oxides of nitrogen (NO_x), respectively, to levels that have essentially required the implementation of aftertreatment systems. This includes diesel particle filters (DPFs) for PM and selective catalytic reduction (SCR) for NO_x .

One of the most important considerations with the implementation of aftertreatment systems is the potential for sulfur to poison the catalyst surface and reduce its efficiency. It is well known, from studies dating back to the 1970s, that the adsorption of sulfur onto a catalyst surface inhibits the performance of the catalyst, leading to increases in overall emissions [1–4]. From a fuel perspective, fuel sulfur is one of the most important properties to control in order to facility low emissions standards. For gasoline vehicles, the reduction of fuel sulfur has been the subject of a number of studies over several decades [5–12]. Further studies have indicated that the sulfur inhibition and subsequent loss of catalyst activity have an effect on all the regulated as well as other emissions under a range of operating conditions, although the sensitivity of various catalyst formulations to sulfur inhibition can vary [13]. More recent studies of gasoline vehicles have focused on other aspects, such as impact of sulfur in terms of immediate impact, the irreversible impact of sulfur due to permanent catalyst damage, the potential for additional emission reductions in lowering sulfur levels below 30 ppm, and the impact of sulfur for Tier 4 vehicles.

The impact of sulfur on diesel aftertreatment systems is also important. A series of studies were conducted to evaluate the potential impact of fuel sulfur on diesel aftertreatment control systems prior to the implementation of the 2007 emissions standards, as part of the Diesel Emission Control – Sulfur Effects (DECSE) project. These studies showed significant sulfur impacts of DPFs, even at sulfur levels as low as 30 ppm, and that the DPF PM conversion efficiency was nearly zero for 150 ppm sulfur fuel. Additional efforts were also undertaken to evaluate the impacts of lubricant sulfur levels on aftertreatment systems as part of the Advanced Petroleum-Based Fuels – Diesel Emission Control project. Fuel sulfur levels were reduced nationwide to 15 ppm.[14–17]

Since sulfur and sulfate are some of the main components of combustion and lubricant-derived particles, it is important to characterize sulfur species to understand the composition and potential health impacts of particles. Sulfate levels in vehicle exhaust particulates can be readily measured, but it is important to understand the relative contribution between combustion and oil-derived particles and the conversion rates found for SO_2 to sulfate. With the low level of sulfur present in the fuel and oil products used in modern vehicles, detection limits in the ppb range are needed to measure the SO_2 contribution. Wet chemical methods are commonly used for the measurement of SO_2 in stationary source applications, and have also been used in applications with vehicle exhaust. This includes the collection of SO_2 using hydrogen peroxide impinger solutions or potassium carbonate coated filters with subsequent analysis by either titration methods or ion chromatography [18–21]. These techniques have limitations for vehicle exhaust as vehicle decline to ultralow emission levels. In particular, such techniques may not provide sufficient detection limits when measured through a

dilution tunnel. For measurements made in the raw exhaust, on the other hand, there are other issues since these techniques provide integrated totals over fixed periods of time that cannot be correlated with exhaust flow rates to determine mass emission rates.

An alternative technique that has been shown to provide real-time, low-level measurement of engine-out SO₂, is differential optical absorption spectroscopy (DOAS). DOAS technology provides the potential for very low detection limits, along with the capability of measuring SO₂ in real-time. DOAS technology has been applied in a number of different applications, including ambient and source measurements and ships. Pisano et al. previously developed and demonstrated a DOAS as part of an earlier study to evaluate the impact of lubricants oil on exhaust emissions. The DOAS developed by Pisano et al. had a time resolution of 3 seconds and an optical path length of 19.6 m, providing a detection limit of 75 ppbv SO₂ at three times the standard deviation of the noise level. These levels were below those of any existing methods at the time for measuring SO₂ in exhaust in real-time. With this detection limit, the contribution of SO₂ from lubricant oil sulfur was measurable over the range of oil sulfur levels utilized in the study [22].

Over the past decade, there have been numerous advances in DOAS technology that have allowed for the development of instruments with lower detection limits in conjunction with smaller sample cells to provide improved residence times. The objective of this study was to construct, test, and provide the ARB with a state-of-the-art DOAS that can measure SO₂ down to 20 ppbV in real-time. The instrument can be used to evaluate the mass balance between SO₂ and sulfate, which provides information about the relative contribution between combustion and lubricant-derived particles. This instrument can provide interesting testing possibilities as ARB seeks to understand the workings of advanced catalyzed aftertreatment systems and their interactions with the fuel/lube systems and the potential to attenuate or produce sulfate particulate matter. This could be of benefit to fuel vs lube oil sulfur contribution assessments, understanding storage vs release of sulfur from catalyzed surfaces, and measuring sulfur fraction partitioning into the PM nucleation particles. The instrument is designed to be run independently in the ARB's laboratories by ARB staff. The system was initially be utilized in the ARB's Heavy Duty Emissions Test Laboratory, but could also be used at ARB's Haagen Smit Laboratory for vehicle test programs involving light duty diesel or gasoline direct injection vehicles. This report describes the DOAS instrument, the results of performance tests, and the installation of the DOAS at the ARB Heavy Duty Emissions Test Laboratory.

2 Theory of DOAS Operation

2.1 Spectroscopy

Spectroscopy can be defined as the investigation of the interaction that occurs between a defined source of electromagnetic radiation and a target sample. The way emissive properties of the radiative source, usually some sort of light source, are perturbed depends upon the sample being investigated. For example, molecules of gas can absorb electromagnetic radiation leading to molecular vibrations or rotations, depending on the absorption frequencies unique to each different type of molecule in the target sample. Therefore, each molecule has its own characteristic absorption pattern over the electromagnetic spectrum. For the investigation of low-level SO₂, the best available spectroscopic technique is Differential Absorption Spectroscopy (DOAS).

Spectroscopic methods evaluate the concentration of the molecule investigated through Beer-Lambert's Law, which states that the fraction of light intensity transmitted through a gas is given by:

$$I/I_0 = \exp(-\sigma(\psi)NL) \quad \text{Equation 2-1}$$

where I and I_0 are the transmitted and incident powers respectively, L is the absorption path length (cms), and N would then be the concentration of the absorbing molecules in number of molecules per cubic centimeter. In this example, $\sigma(\psi)$ is the wave-number dependent absorption cross section in square centimeters per molecule.

2.2 DOAS (Differential Optical Absorption Spectroscopy)

Differential Optical Absorption Spectrometry (DOAS) is a UV/VIS optical measurement technique based on Beer-Lambert's Law. Since absorption coefficients in the UV are generally orders of magnitude higher than in the IR region, sensitivity is usually enhanced, which makes DOAS a method for measuring relatively low concentrations. On the other hand, UV absorption features are much broader than those typically associated with the infrared spectra, which leads to two potential problems:

- 1) Only species with absorption features that are considerably narrower than the typical measuring window of 15–40 nm can be detected and quantified; this constraint significantly reduces the number of compounds that can be measured.
- 2) The light intensity without absorbing species in the optical path, I_0 , has to be known to apply Beer-Lambert's Law. Broad absorption features are affected by numerous species in the light path, and with light scattering are often indistinguishable from the background, making it difficult to measure I_0 .

One approach to address potential problems incorporates differential optical absorption, in which I_0 is replaced by I'_0 , where I'_0 is the light intensity in the absence of a structured absorption band (refer to Figure 2-1). The DOAS technique solves for the concentration using a modified form of the Beer-Lambert's Law, in which a differential absorption coefficient $[\epsilon']$ replaces the absolute absorption coefficient $[\sigma(\psi)]$. C is the species concentration, L is the optical path length, and I is the intensity at an absorption peak.

$$C = \frac{1}{\epsilon' \cdot L} \ln \frac{I'_0}{I} \quad \text{Equation 2-2}$$

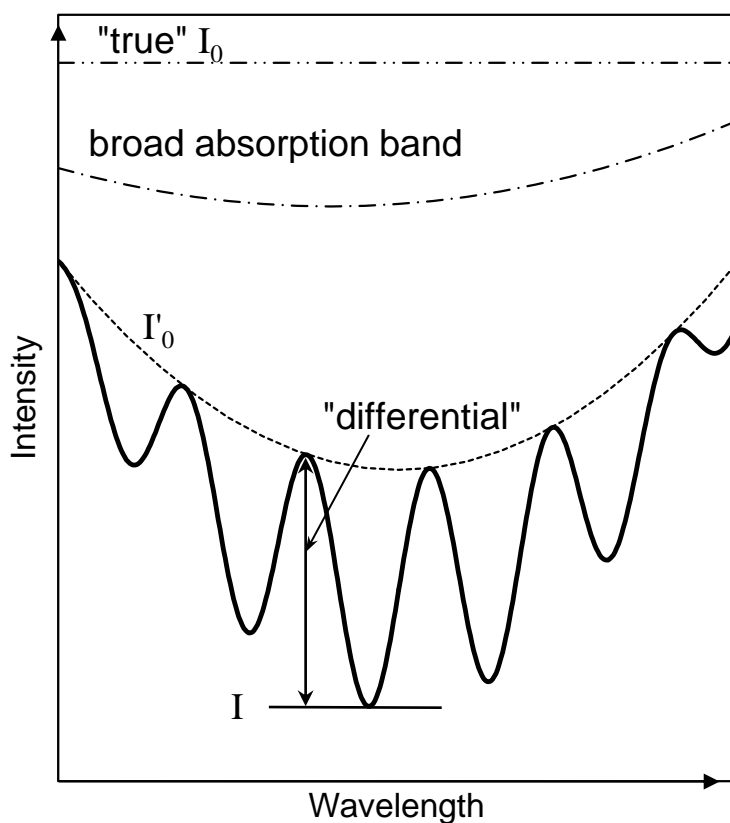
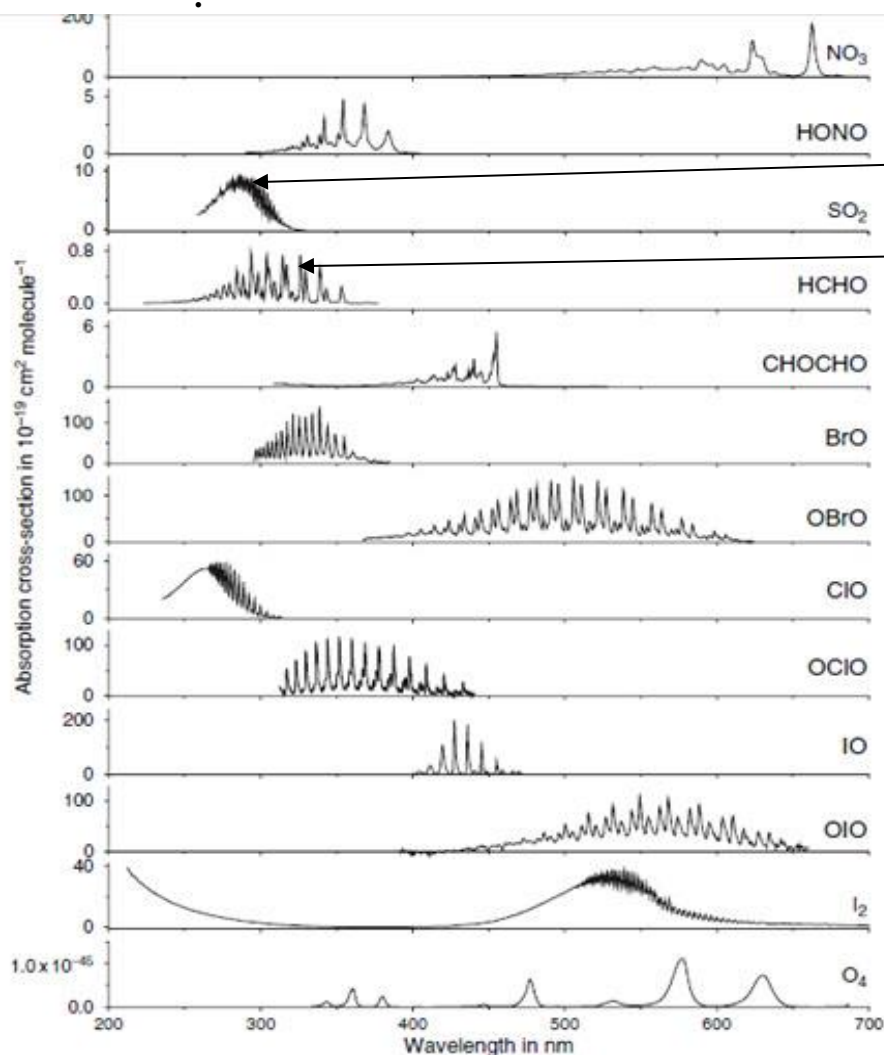


Figure 2-1 DOAS technique, in which I_0 is replaced by I'_0 , the light intensity in the absence of a structured absorption band

2.3 List of Pertinent Species Capable of Being Measured By DOAS

There are many gases, with UV-vis signatures, to which the DOAS method can be applied, including HCHO, NH₃, NO and NO₂ for automotive applications. The absorption cross sections for a range of species are provided in Figure 2-2. Developing the DOAS method for different species is primarily a question of software development; however, an additional consideration is tailoring the light source to the desired species for better sensitivity and also examining potential interferences. For example, there is some overlap of the spectral absorption cross-section between SO₂ and HCHO, as is evident from Figure 2-2.



Plot shows spectral response of SO_2 and HCHO , which are cross-over species and need to be both accounted for in the method development for this proposed SO_2 DOAS.

Figure 2-2 Absorption cross-sections of typical species measured by the DOAS technique; note SO_2 and HCHO responses which are highly important for the proposed DOAS system

The spectral range selected for the designed DOAS was 200-230 nm, to avoid possible interferences from other exhaust constituents. A closer view of the absorption cross sections in this region is provided in Figure 2-3. It can be seen that in this region that while the absorption cross section for SO_2 is still fairly strong, this is a weak absorption region for HCHO . Thus, HCHO concentration would likely have to be 100 times higher in concentration than SO_2 to interfere. In this region, it is also known that both NO and NH_3 absorb and they will be measured concurrently with SO_2 , however, their cross-sections are also typically much weaker (100 times or more).

Region for enhanced grating response 210 to 230 nm. Far more sensitive to SO₂ than HCHO

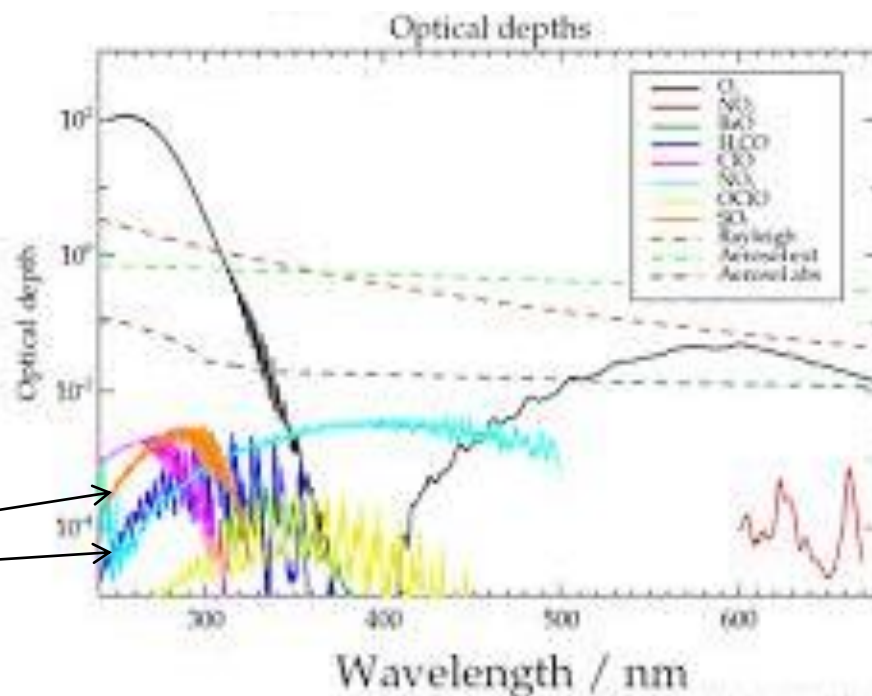


Figure 2-3. Absorption cross-sections overlapped of typical species measured by the DOAS technique; note SO₂ and HCHO responses which are highly important for the designed DOAS system

3 Description of DOAS Instrument

The differential optical absorption spectrometer (DOAS) developed for this project was specially designed and built for rapid, extractive detection of sulfur dioxide at low ppb levels for the ARB. The integrated system consists of the extractive sampling train, the sampling cell, and the spectrometer. An overall schematic layout of the system is shown in Figure 3-1, and a full explanation of the system follows.

DOAS Extractive analyzer layout

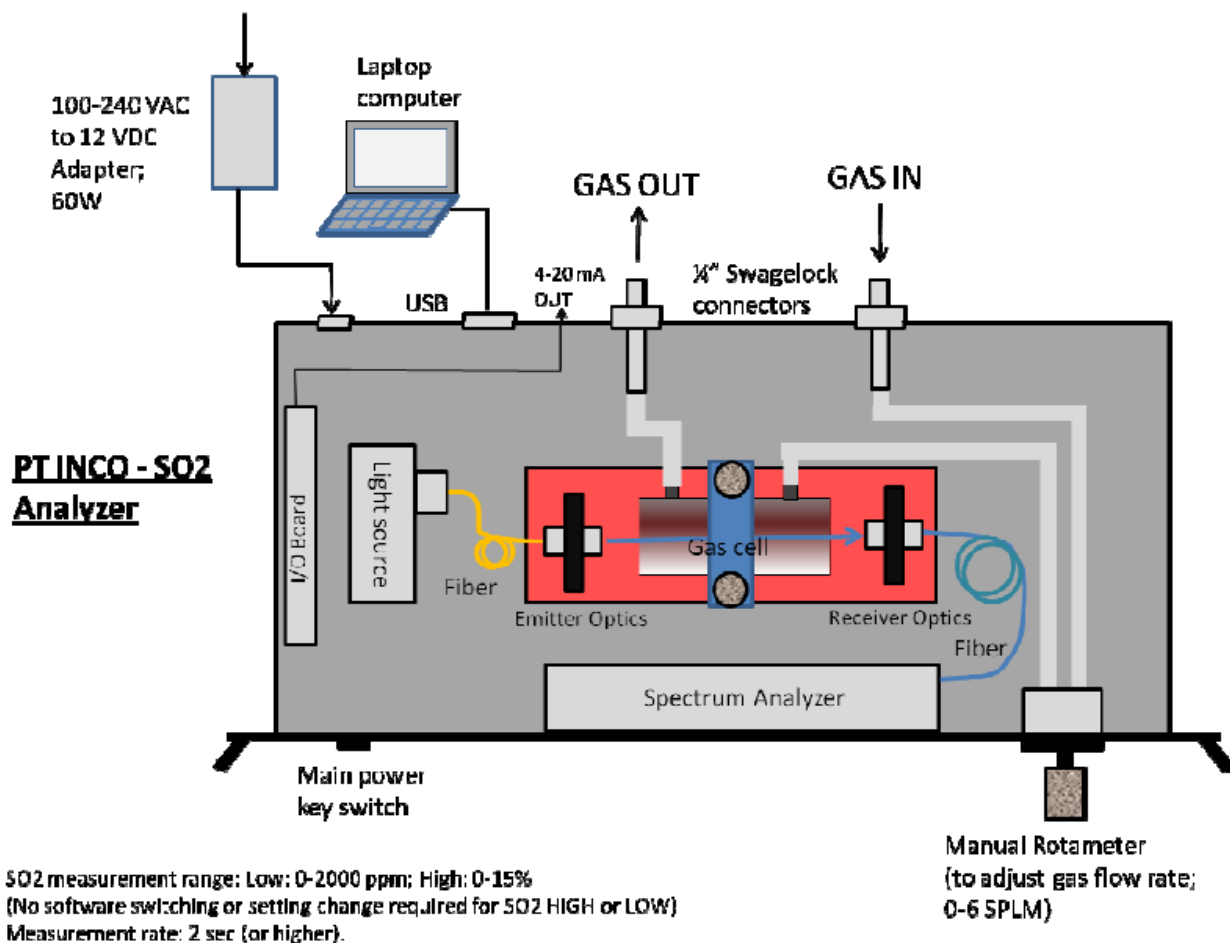


Figure 3-1. Components of the DOAS system developed for the measurement of low level (~20 ppbV) SO₂ from vehicle exhaust

To measure reactive molecules, such as SO₂, as well as to allow fast response times, the residence time in the sample cell, and thus the volume of the cell, was made as small as possible. The sample cell uses a single-path design with beam expanding and focusing optics to minimize cell volume. Since exhaust gases are very corrosive, hot, and humid, and potentially contain higher levels of particles, direct exposure of the mirrors to the sample gas was avoided. Therefore, the cell was designed as an open cell with the sample cell residing between the windows, rather than having the transmitting and collecting optics inside the sample cell. The sample cell is constructed of electro-polished 316 SS for inertness, with an inlet and outlet provided for the sample gas. The sample cell is equipped with coated anti-reflective quartz windows at each end to allow the UV light to enter and exit. Quartz windows were used with the sample cell, since they are easy and fast to remove and clean.

The sample cell for the UC Riverside system is cylindrical with a length of 1.0 m. The total volume of the DOAS sample cell is approximately 0.51 liters. The cell is designed to operate over a full 8-10 hour testing day at a temperature of 110°C, with a temperature range from 25°C up to 120°C (250°F). The cell is heated radiatively with heating tapes and the temperature is maintained with heating tapes. A tunable PID controller maintains the cell temperature at a user-defined level. During operation, gas pressure inside the sample cell is slightly below atmospheric due to the extractive sampling technique.

A specially ordered deuterium lamp was used as the light source for the 200–230 nanometer (nm) region. The spectral output of this light source was tested and shown to drop off significantly below 230 nm. The UV lamp transmitter is shown in Figure 3-2.

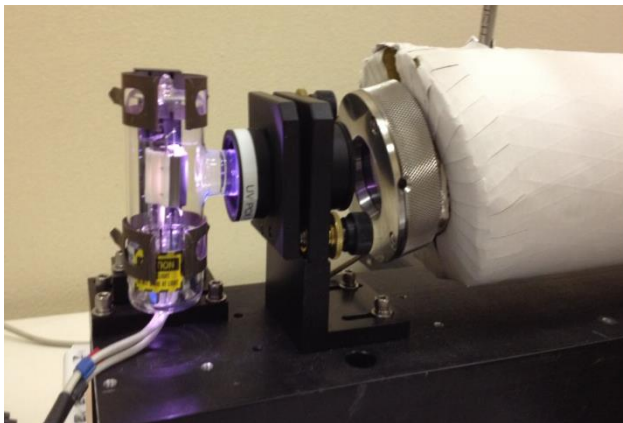


Figure 3-2. UV lamp and transmitter

The spectrometer/receiver consists of a single working element, a concave 1200 groove/millimeter (mm) holographic diffraction grating optimized for 200–230 nm. The spectrometer is shown in Figure 3-3. The concave diffraction grating both wavelength-disperses the light and focuses it onto the single-stage, thermoelectric-cooled, charge-coupled device (CCD) detector array. The effective resolution of the spectrometer is ~0.1 nm. Spectra are measured every 0.25 milliseconds (ms), and are integrated over 5 seconds for each sample point. The optical elements windows, transfer optics, collector optics and retroreflector are integrated with the spectrometer to provide yield capture efficiencies of greater than 80%.

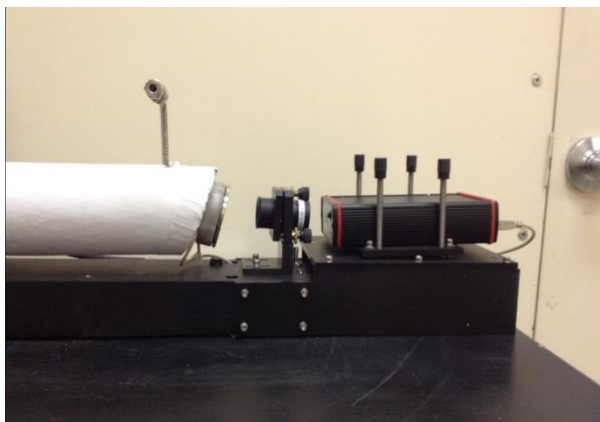


Figure 3-3. DOAS receiver, with grating

The DOAS is designed to be attached via a sampling train to a sample port from the vehicle's exhaust system. A pump can be used to extract the vehicle/engine exhaust through the sampling train and the DOAS. Typical elements of a sampling train include a heated particle filter (300°F; 150°C) and a heated PFA-line (300°F; 150°C). Care should be taken to avoid any cold spots in the sampling path. All interior surfaces of the sample train should be either stainless steel or PFA teflon, with the exception of the particle filter, which could consist of a material such as bonded quartz fibers.

The DOAS software, LasIRView 2009, is a user-friendly Windows-based package with outputs for data logging and a software manual. The software provides data outputs via ethernet or RS-232 for easy incorporation into CARB data logging requirements, as well as 4-20 mA output for up to 4 parameters. The program communicates directly with analyzer so users can monitor the analyzer in realtime. The program has various functions including laser setup, location setup, sensor input setup, background subtraction, various correction setting and data processing, etc. The basic package does not have additional analog inputs to record such items as speed, exhaust flow, or pressures from other sources (which would be provided by the ARB).

The following has been provided and tested:

- 1) Fiber optic link to extractive cell
- 2) AC-DC power supply
- 3) A heating control for the sample cell, including thermal sensors and thermal controllers, as the sample cell will be heated above the dew point of typical vehicle exhaust. The DOAS method is written for the sampling temperature and has a thermal correction curve for the various temperatures selected. Temperature directly affects both the line strength of the molecule investigated as well as the number of molecules being counted via the ideal gas law correction.
- 4) A pressure transducer for pressure input into the system analyzer, which in turn provides input for the software to correct for pressure variations of the spectral response. The system is designed for the signal specific to the pressure transducer for the sample cell.
- 5) Launch and receive optics to couple the UV spectrometer to the cell
- 6) System analyzer, including a laptop computer for display and control functions
- 7) DOAS vehicle exhaust-specific software with method written for the analysis of low level SO₂ in the presence of typical diesel exhaust streams. Windows-based software will be installed on a laptop that will be provided by the ARB.
- 8) The DOAS will be transportable, so that it can measure either engine out or dilution tunnel values, as well as be moved to other labs within the ARB.

4 Test Laboratory Configuration

Prior to installation at the ARB facility, the proposed DOAS will be evaluated at UC Riverside. Testing will be done at a UC Riverside laboratory specifically designed for evaluating spectroscopic instruments – a laboratory initially funded by the Electric Power Research Institute (EPRI) for the evaluation of commercially available spectroscopic instruments that measure flue gases typical of combustion boilers (gas turbine, coal, and wood). The following section provides a description of the test facility. Pictures of the DOAS in the test laboratory are provided in Figure 4-1 and Figure 4-2.

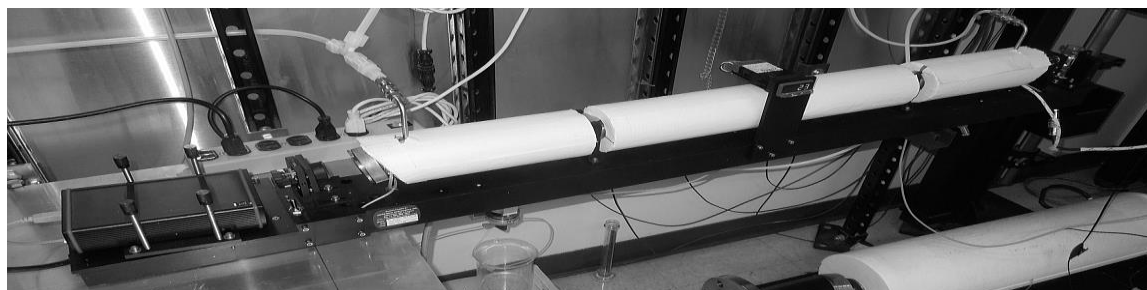


Figure 4-1. DOAS in the Laboratory at UC Riverside



Figure 4-2. Overview picture of DOAS in the Laboratory at UC Riverside

Sample Cell Measurements

Since the DOAS is an extractive system the laboratory was equipped with a calibrated source that provided a constant flow through the extractive cell of 7.5 slm. The source of the gas was from the TECO 42 dilution calibrator.

Calibration and Gas Delivery System

The Laboratory employs a TECO 146C Dynamic Gas Calibrator with central processor unit (CPU) and controlled precision mass flow controllers. The calibration system provides precise concentrations of target gas by utilizing gas dilution, through a precision, low flow mass flow controller. For the proposed project, a supply of “zero” air is required to dilute the higher concentration calibration gases in order to attain the target gas concentration to be delivered to the sample cell. Zero air refers to the purity of the diluent gas, indicating a non-detectable concentration of the species under investigation.

The system flow rates are determined by the CPU from the electrical signals from each mass flow controller. The CPU calculates the necessary flows to attain the desired pollutant concentration. Equation 3-1 is used to calculate the required zero air and pollutant gas flows.

$$C_f = C_i * \{Q_{\text{gas}} / (Q_{\text{gas}} + Q_{\text{air}})\}$$

Equation 3-1

Where: C_f = final concentration of the diluted gas
 C_i = source gas concentration
 Q_{gas} = volumetric flow rate of the source gas
 Q_{air} = volumetric flow rate of the zero air source

The mass flow controller used to control the diluent air has a higher volume capability (approximately 1.8 scfm (50 slpm)) than the mass flow controller used to control the source gas (approximately .0036 scfm (0.1 slpm)). This approach allows the control system to develop a broad range of gas concentrations, from trace amounts to high concentrations, limited only by the initial NIST traceable gas source concentration. The measured gas species and the high flow diluent are mixed in an inert (Teflon[®]) chamber prior to entering the exhaust manifold. The uncertainty of the calibration source is dependent primarily on the accuracy of the TECO 146C calibrator. The calibrator has a purported accuracy of better than 2% of the full scale reading.

The gas supply consisted of a single certified SO₂ cylinder with concentration of 96.3 ppmV, which was mixed at different ratios with zero air, at two predetermined dilution flow rates, to achieve the desired concentrations. The nominal concentrations for the SO₂ measurements are listed in Table 4-1 for the low dilution (9500 cc/min) and Table 4-2 for the high dilution (47,500 cc/min) to encompass a range from 20 ppbV (low detection) to 953 ppbV (high detection). Two concentrations were tested for both dilution flows (i.e., 51 and 151 ppbV) to provide data for overlapping concentrations under each of the dilution conditions. These are highlighted by being in italics in the two tables. Other calibration gases were National Institute of Standards and Technology (NIST) certified gas cylinders, each containing concentrations of the target species in an inert (nitrogen) carrier. The gas standards were certified by Scott Marrin Gases, and a supplier's certification sheet was obtained for each of the gases purchased.

Dilution	SO ₂ Cylinder	Total	Dilution	SO ₂	SO ₂
Flow	Flow	Air Flow	Ratio	Concentration	Concentration
(cc/min)	(cc/min)	(cc/min)		(ppmV)	(ppbV)
9500	96.0	9596.0	9.90E-03	0.953	953
9500	75.7	9575.7	7.83E-03	0.754	754
9500	55.6	9555.6	5.76E-03	0.554	554
9500	35.4	9535.4	3.67E-03	0.353	353
9500	25.4	9525.4	2.62E-03	0.253	253
9500	20.4	9520.4	2.10E-03	0.202	202
9500	15.3	9515.3	1.58E-03	0.152	152
9500	10.4	9510.4	1.05E-03	0.101	101
9500	5.4	9505.4	5.26E-04	0.051	51

Table 4-1. SO₂ test concentrations used for low dilution

Dilution	SO ₂ Cylinder	Total	Dilution	SO ₂	SO ₂
Flow	Flow	Air Flow	Ratio	Concentration	Concentration
(cc/min)	(cc/min)	(cc/min)		(ppmV)	(ppbV)
47500	96.0	47596.0	2.00E-03	0.192	192
47500	75.7	47575.7	1.58E-03	0.152	152
47500	55.6	47555.6	1.16E-03	0.111	111
47500	35.4	47535.4	7.36E-04	0.071	71
47500	24.4	47524.4	5.26E-04	0.051	51
47500	15.3	47515.3	3.16E-04	0.030	30
47500	10.4	47510.4	2.10E-04	0.020	20

Table 4-2. SO₂ test concentrations used for high dilution

5 Performance Tests at UC Riverside

The following section provides an overview of the results of the laboratory testing that was conducted at UC Riverside. This included tests to determine the minimum detection limits of the system, tests to evaluate the linearity of the system, and test to evaluate the potential impact of interferences on the SO₂ measurements.

5.1 Minimum Detection Limits

According to the accepted convention the limit of detection (LOD) is the lowest analyte concentration that is significantly different from the blank which is a known sample that does not have any of the analyte (basically zero).

The signal intensity (y_D) corresponding to the detection limit represents the size of the signal that is equivalent to the blank value.

The signal is determined by the mean value μ_b and the standard deviation σ_b of a blank signal described in equation (1), (Grant et al, 1992)

$$y_D = \mu_B + K_D \sigma_b \quad (1)$$

where $K_D = 3$.

Measurements at a full range of SO₂ concentrations are shown in Table 5-1 and Table 5-2. These measurements include the target concentration, the measured concentration, the measured concentration corrected for background, and the standard deviation of the measurements over 10 minutes. The results show a standard deviation at the blank level of 4 ppbV and 5 ppbV, respectively, for the low and high dilution measurements. Based on these measurements, the minimum detection limits are approximately in the range of 12 to 15 ppbV. It should be noted that similar are lower standard deviations are found for the higher concentrations, indicating a roughly similar level of detection throughout the measurement range evaluated.

Dilution	SO ₂	SO ₂ DOAS	SO ₂ DOAS	Standard	Correlation
Flow	Concentration	Concentration	Concentration	Deviation	Coefficient
(cc/min)	Calibrator	raw 5- second	5-sec with bkg sub	10 min	R ²
	(ppbV)	(ppbV)	(ppbV)	(ppbV)	
9500	953	940	945	1.6	0.99
9500	754	745	750	2.2	0.99
9500	554	545	550	1.9	0.98
9500	353	342	347	2.2	0.97
9500	253	244	249	1.7	0.96
9500	202	192	197	2	0.95
9500	152	142	147	1.9	0.94
9500	101	93	98	2	0.85
9500	51	42	47	3	0.64
9500	0	-5	0	4	0.14

Table 5-1. SO₂ low dilution concentration measurements

Dilution	SO ₂	SO ₂ DOAS	SO ₂ DOAS	Standard	Correlation
Flow	Concentration	Concentration	Concentration	Deviation	Coefficient
(cc/min)	Calibrator	raw 5- second	5-sec with bkg sub	10 min	R ²
	(ppbV)	(ppbV)	(ppbV)	(ppbV)	
47500	192	185	191	5	0.96
47500	152	148	154	5	0.93
47500	111	102	108	2.1	0.87
47500	71	64	70	4	0.71
47500	51	43	49	3	0.57
47500	30	20	26	5	0.36
47500	20	11	17	2	0.23
47500	0	-6	0	5	0.11

Table 5-2. SO₂ high dilution concentration measurements

5.2 Linearity Tests

Additional tests were conducted to evaluate the linearity of the systems over a range of concentrations for both low and high dilution conditions. The data for these tests are tabulated in Table 5-3 and Table 5-4 and shown graphically in Figure 5-1 and Figure 5-2. The tests showed good linearity over the concentration ranges for both the low and high dilution measurements, respectively. The slopes for the low and high dilution measurements were 0.995 and 1.011, respectively, and R² values of 0.999 and 1.0, respectively.

Dilution	SO ₂ Cylinder	Total	Dilution	SO ₂	SO ₂
Flow	Flow	Air Flow	Ratio	Concentration	Concentration
(cc/min)	(cc/min)	(cc/min)		(ppmV)	(ppbV)
9500	96.0	9596.0	9.90E-03	0.953	953
9500	75.7	9575.7	7.83E-03	0.754	754
9500	55.6	9555.6	5.76E-03	0.554	554
9500	35.4	9535.4	3.67E-03	0.353	353
9500	25.4	9525.4	2.62E-03	0.253	253
9500	20.4	9520.4	2.10E-03	0.202	202
9500	15.3	9515.3	1.58E-03	0.152	152
9500	10.4	9510.4	1.05E-03	0.101	101
9500	5.4	9505.4	5.26E-04	0.051	51

Table 5-3. SO₂ low dilution concentration linearity measurements

Dilution	SO ₂ Cylinder	Total	Dilution	SO ₂	SO ₂
Flow	Flow	Air Flow	Ratio	Concentration	Concentration
(cc/min)	(cc/min)	(cc/min)		(ppmV)	(ppbV)
47500	96.0	47596.0	2.00E-03	0.192	192
47500	75.7	47575.7	1.58E-03	0.152	152
47500	55.6	47555.6	1.16E-03	0.111	111
47500	35.4	47535.4	7.36E-04	0.071	71
47500	24.4	47524.4	5.26E-04	0.051	51
47500	15.3	47515.3	3.16E-04	0.030	30
47500	10.4	47510.4	2.10E-04	0.020	20

Table 5-4. SO₂ high dilution concentration linearity measurements

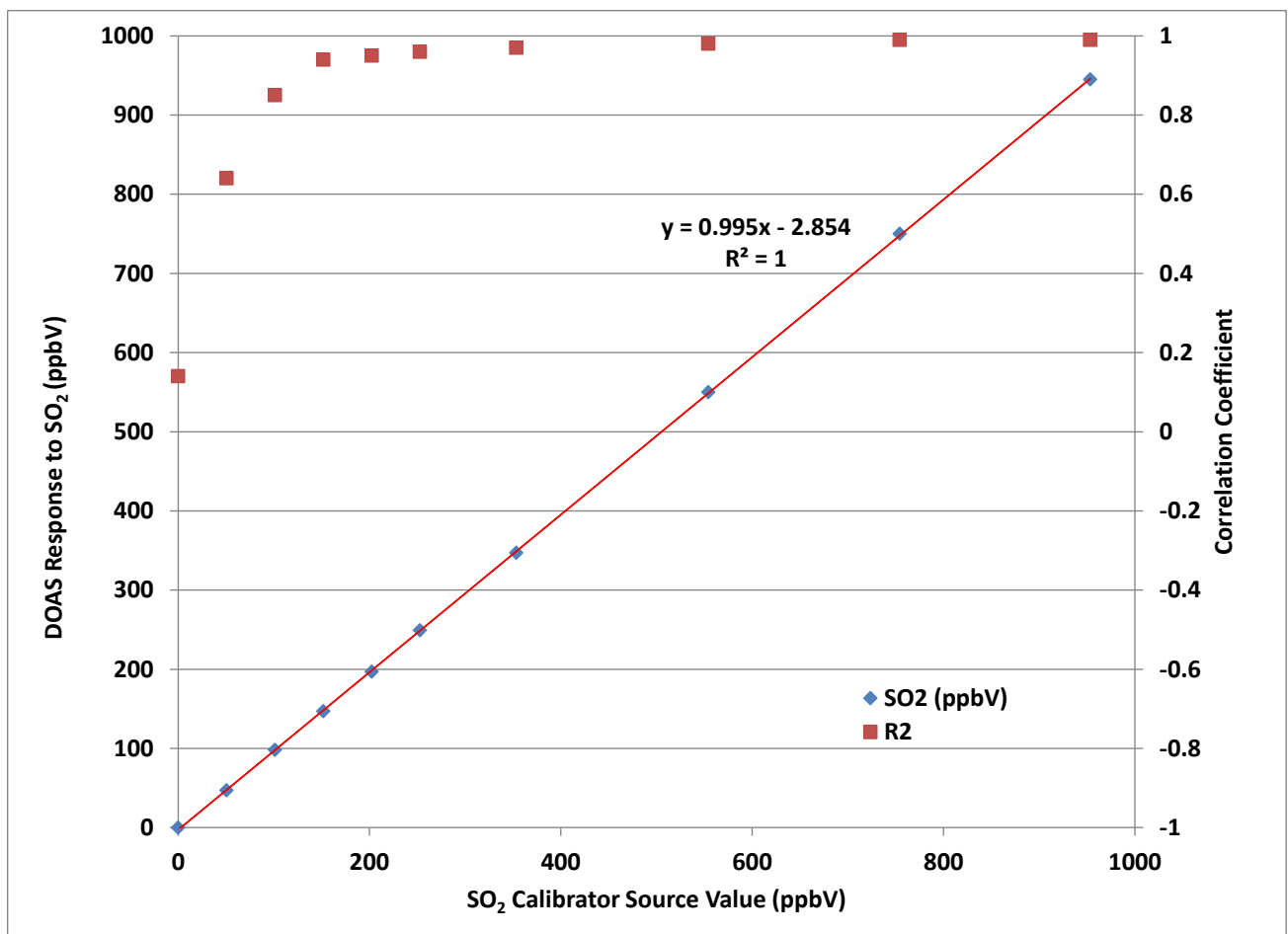


Figure 5-1. DOAS SO₂ low dilution linearity plot

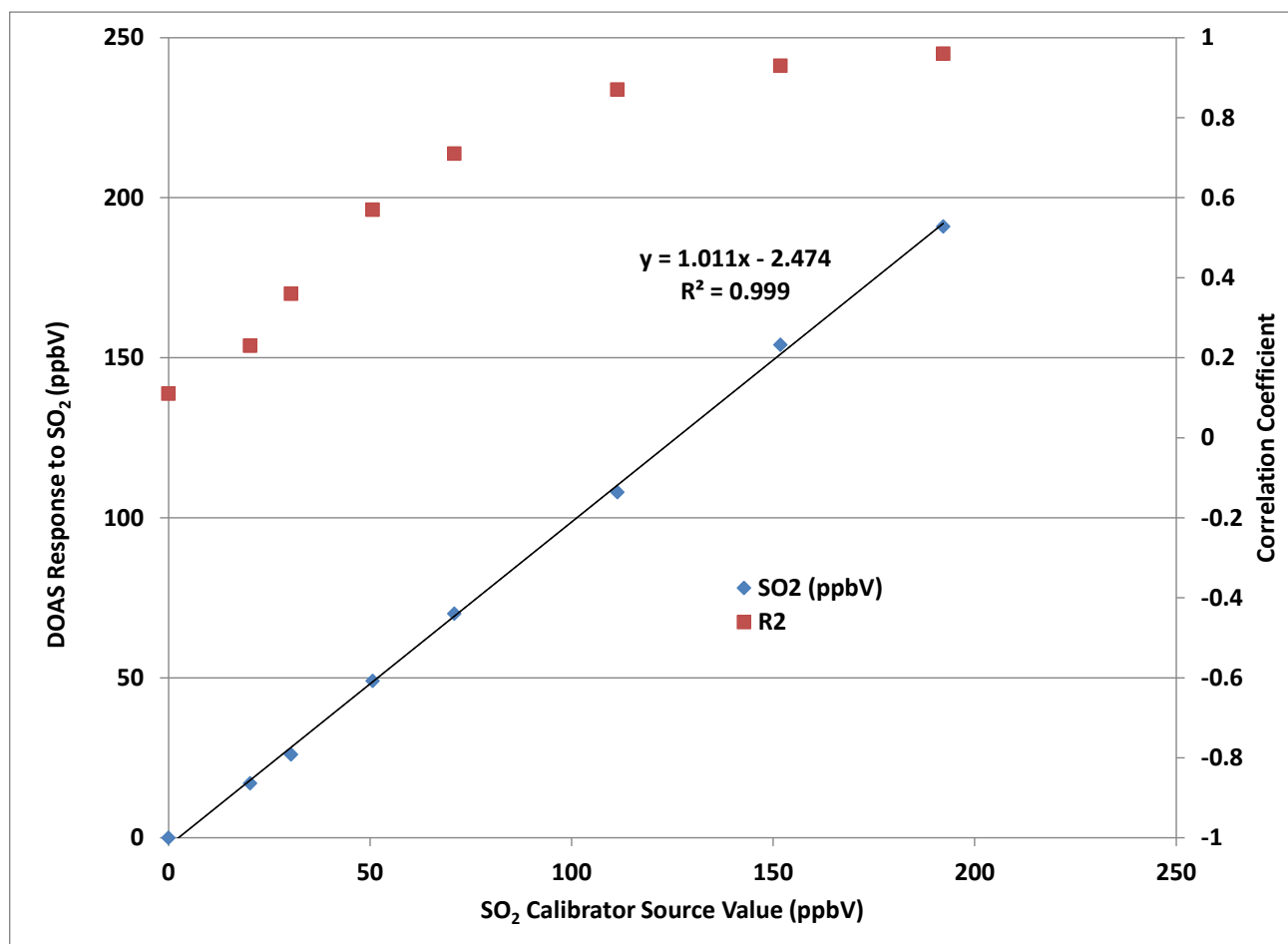


Figure 5-2. DOAS SO₂ high dilution linearity plot

5.3 Interference Tests

A series of tests were conducted to evaluate potential interferences with the SO₂ absorption. This included tests with different concentrations of SO₂ with NO and NH₃. The results of these tests are provided in the following subsection.

The initial configuration files of the three species, SO₂ (Figure 5-3), NO (Figure 5-4) and NH₃ (Figure 5-5), show that the spectral range of measurement was from 203 nm to 230 nm. This range was chosen as it encompasses the best available spectral range for SO₂ measurements, with regard to sensitivity. Note on the figures, the reference spectra are in red and the measured spectra are in blue, with all tests were done with the instrument configured for 5 second response. Also note on Figure 5-4, that there is a strong NO absorption starting at 214 nm and ending at 216 nm, which will likely interfere with the SO₂ response. For NH₃ (Figure 5-5), the strongest absorption occurs from 203 nm to 204 nm. Although this absorption is significantly weaker than that of SO₂, it is still a likely interferent.

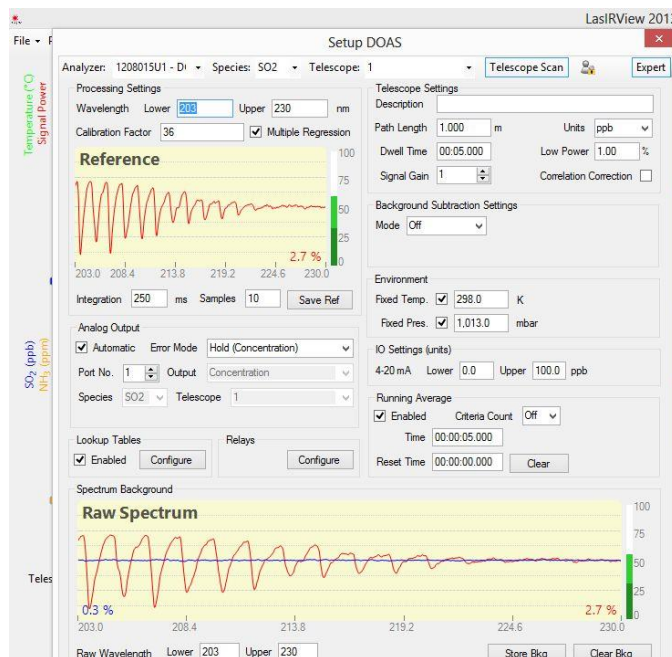


Figure 5-3. Shows initial DOAS configuration file and reference spectra for SO₂.

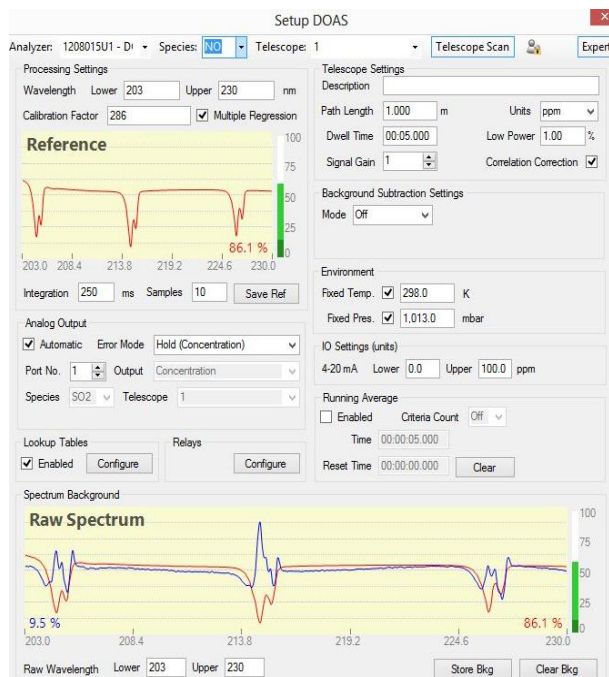


Figure 5-4. Shows initial DOAS configuration file and reference spectra for NO, notice strong NO absorption from 214 nm to 216 nm.

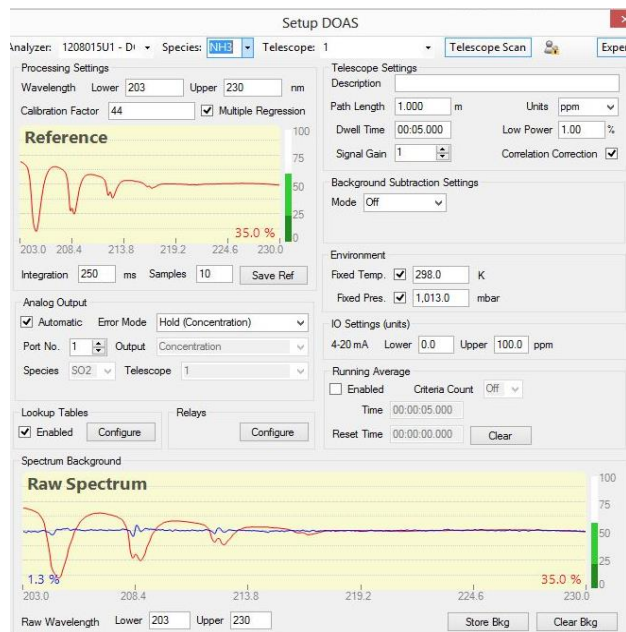


Figure 5-5. Shows DOAS configuration file and reference spectra for NH_3 where the strongest absorption is.

Initial tests were done to measure the backgrounds of SO_2 , NO , and NH_3 by running zero air through the sample cell. Note that all measurements are with a 250 ms response time integrated for a period of 5 seconds. Figure 5-6 shows the background spectra and values for the three species, with SO_2 being around -5 ppbV, and NO being less than 0.000 ppmV and NH_3 being -0.0055 ppmV. These backgrounds were measured during the linearity tests and were reproducible over both dilution ranges.

In Figure 5-7, the SO_2 spectra is enlarged to show that the background is flat over the entire range of measurement (203 nm to 230 nm). Also note that the background in this case was -3.4 ppbV, standard deviations over this test period (over an hour) were 4.3 ppbV, yielding a minimum detection limit (MDL) of 12.9 ppbV at 3 times the standard deviation of zero air response.

Ozone is also measured since it is in the spectral region and is presented here on the plots. Ozone is included since the instrument can currently measure up to four species. We expect that the ozone will be replaced with HCHO once we have conducted the work for the HCHO response and interference testing. Since the HCHO response drops off significantly over this range, we do not expect a significant interference contribution from HCHO .

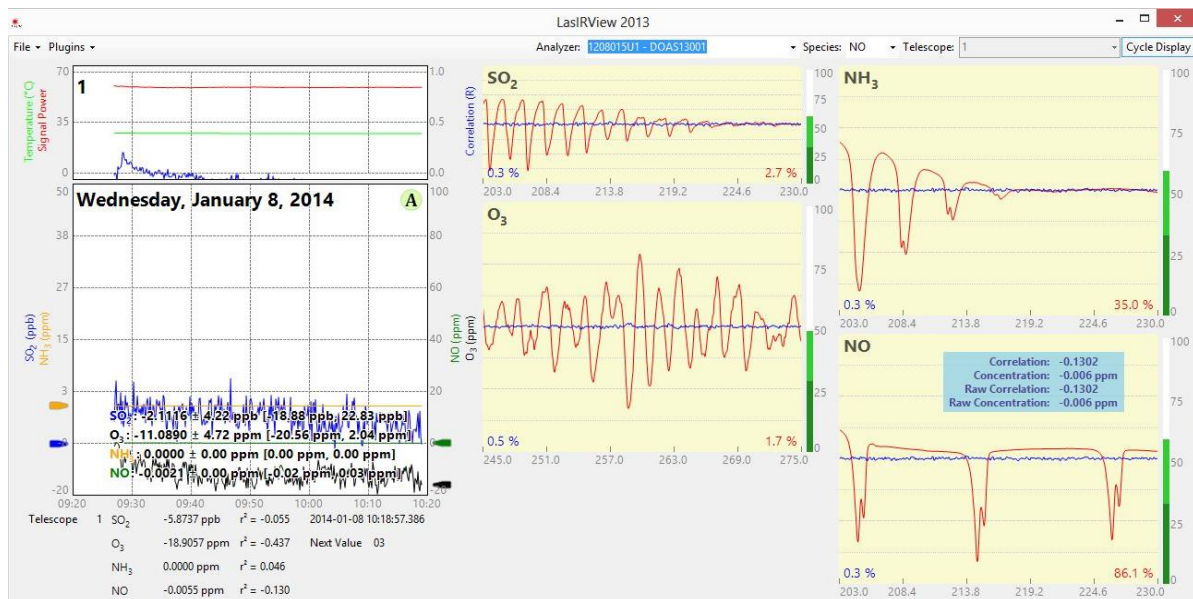


Figure 5-6. Shows DOAS SO₂, NH₃ and NO 5-second background response with only zero air flowing. Notice measured SO₂ background is slightly negative (-5 ppbv) with standard deviations between 4-5 ppbV.

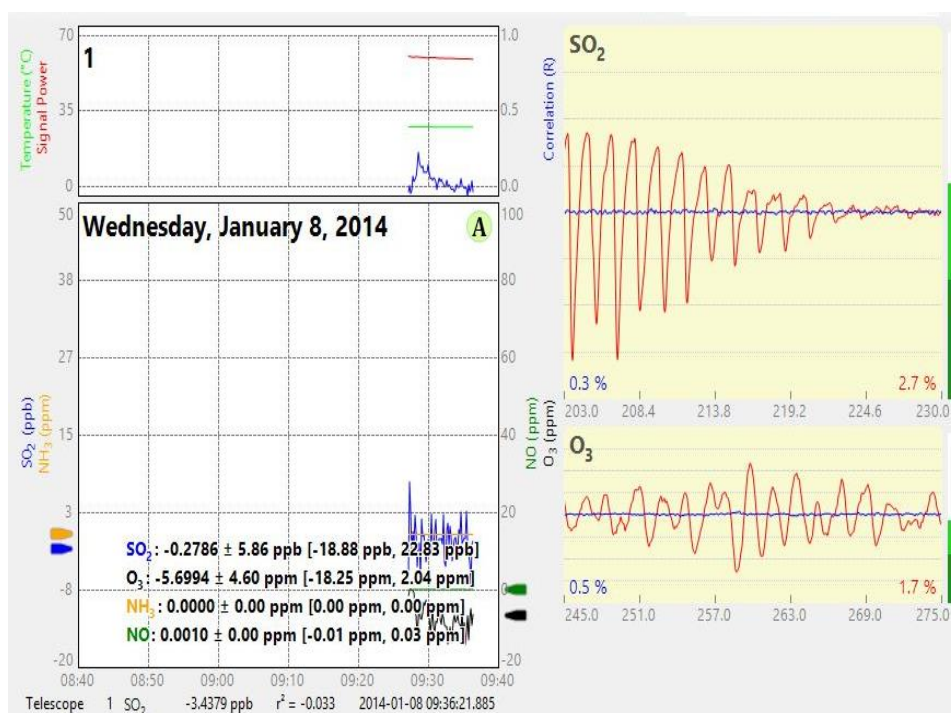


Figure 5-7. Shows enlarged DOAS SO₂ 5-second background response with only zero air flowing. Notice measured SO₂ background again is slightly negative (-3.4ppbv) with standard deviations again between 4-5 ppbV.

The next two figures, Figure 5-8 and Figure 5-9, show the DOAS response to two discreet levels of SO₂ calibration gas. One is at 80 ppbV (Figure 5-8) and the other is at 680 ppbV (Figure 5-9).

Note that the response to the SO₂ gas does not affect the background levels of either NH₃ or NO, so basically at this level of SO₂ there is no interference to either NO or NH₃.

For Figure 5-8, looking at the measured (blue) response, it can be seen that other than for SO₂ it is a flat line for NH₃ and NO. Although the measured line for SO₂ is fairly weak (just 5 times over the detection) line, the correlations were typically between 0.55 and 0.75 at this level. Again it is important to point out that this is with a 5 second integration and with longer integration times the sensitivity would improve.

Looking at Figure 5-9, where 680 ppbV of SO₂ is being injected, the response of the measured signal (blue) more closely matches the reference (red), and correlations are much higher, typically greater than 0.85 and approaching 1.0 on occasions. Also, note that the response to the SO₂ gas does not affect the background levels of either NH₃ or NO at this higher level of SO₂, so there is not expected to be any interference to either NO or NH₃ over the expected range of SO₂ measurements.

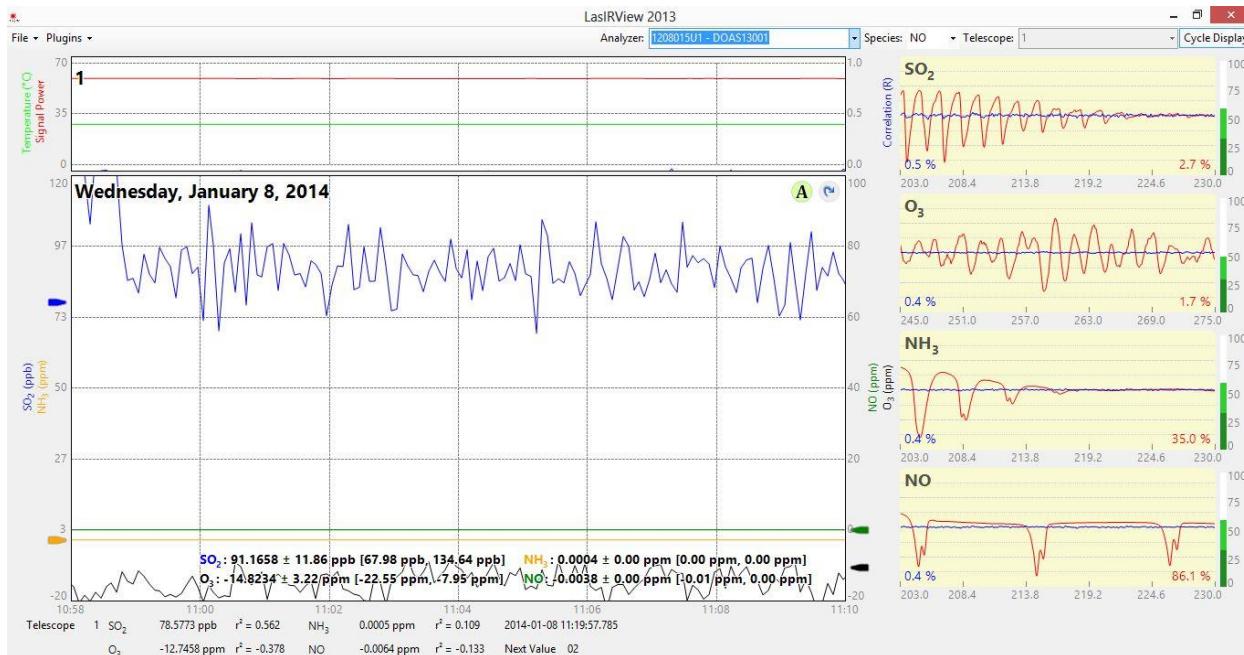


Figure 5-8. Shows DOAS SO₂ 5-second response at 80 ppbV, notice that NH₃ and NO spectra and response are unaffected by this level of SO₂.

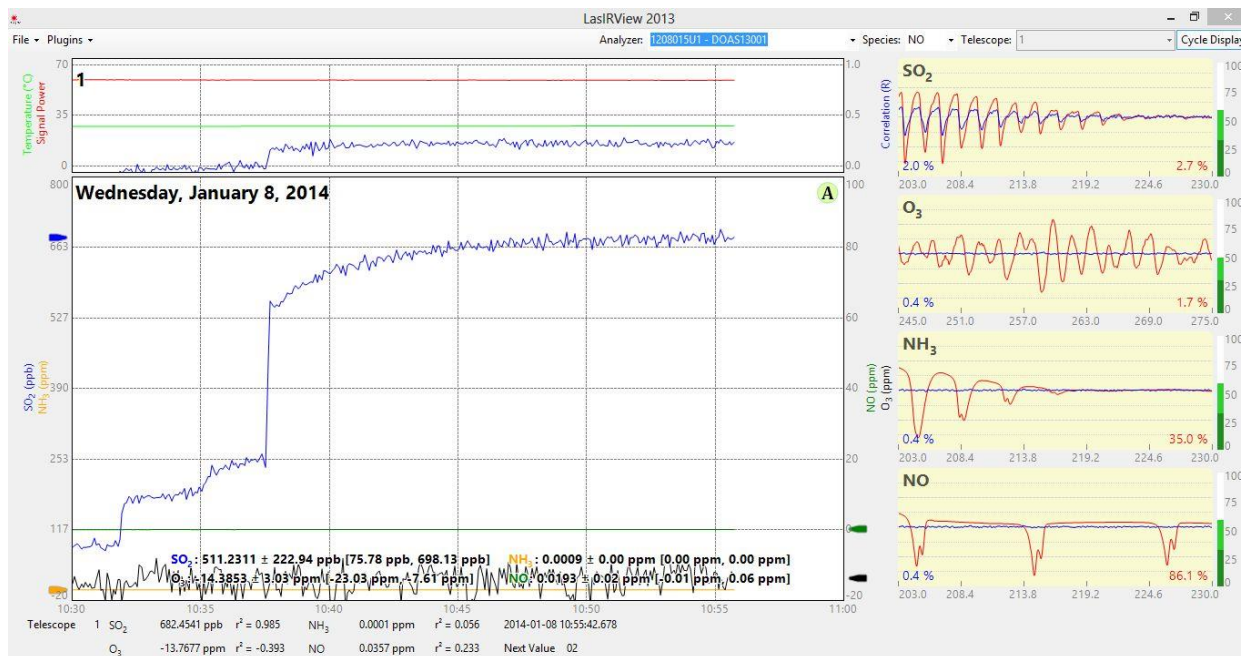


Figure 5-9. Shows DOAS SO₂ 5-second response at 680 ppbV. Notice that NH₃ and NO spectra, as in the case of the 80 ppbV of SO₂, have responses that are unaffected by this level of SO₂.

Initial tests at 300 ppmV of NO and 16.6 ppmV of NH₃ confirmed that at these high levels they would interfere with the SO₂ response over the spectral range specified. At 300 ppmV of NO, the SO₂ interference response was at levels higher than 100 ppbV. At 16.6 ppmV of NH₃, the SO₂ interference response was between 20-25 ppbV.

Given these results, the spectral range of measurement was changed from (1) to (2)

- 1) 203 nm to 230 nm
- 2) 206 nm to 214 nm

Refer to Figure 5-10 which shows the revised configuration file for SO₂, as well as the spectra (reference in red) for the narrower region.

Figure 5-11 shows DOAS SO₂ response being less than 1.5 ppbV with 300 ppmV of NO injected with the new spectral range of analysis.

Figure 5-12 shows DOAS SO₂ response being less 8 ppbV with 16.6 ppmV of NH₃ injected with the new spectral range of analysis.

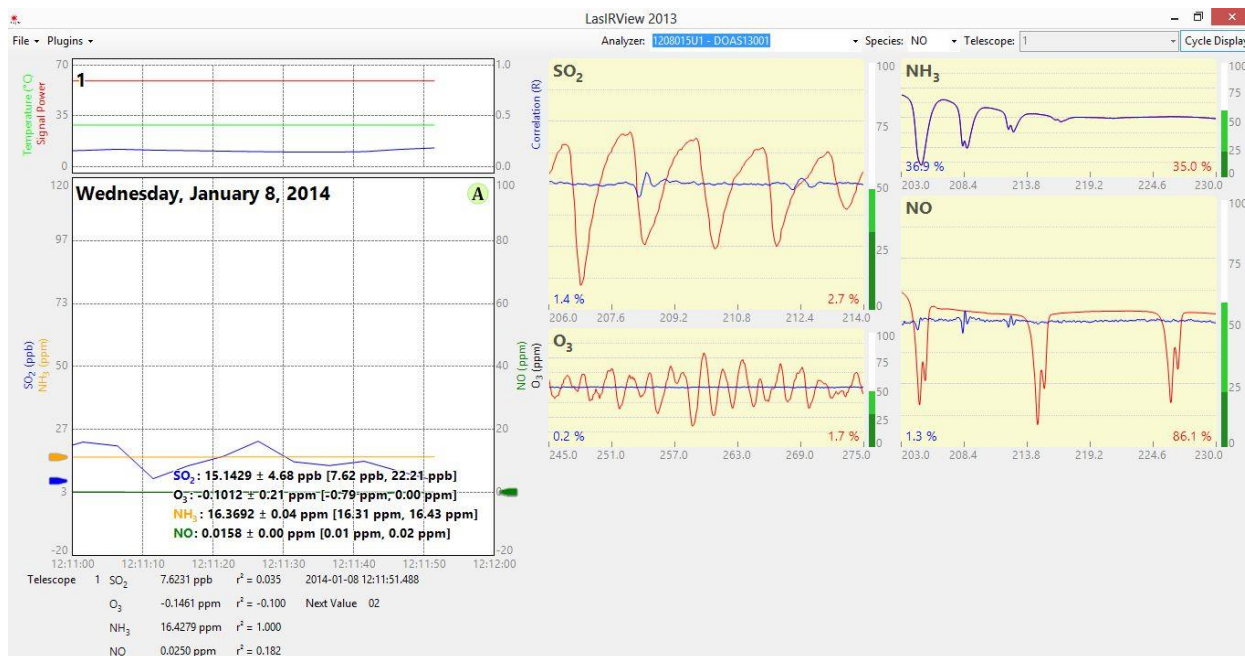


Figure 5-12. Shows DOAS SO₂ 5-second background response with new fit limits to minimize NH₃ as well as NO interferences. In this example 16.5 ppmV of NH₃ is injected. Notice strong measured spectral lines for NH₃ where the blue line (measured) lays on top of the red line (reference). The interference to SO₂ at this NH₃ level is between 5-10 ppbV.

To confirm that the new spectral range of analysis yielded a similar overall response to the target gases, measurements were again conducted at 80 ppbV and 680 ppbV of SO₂. Figure 5-13 shows the response with the original spectral fit, and Figure 5-14 shows the response with the new spectral fit which minimizes interferences for the 680 ppbV test. Note that the measured values for both analysis yielded similar results.

Additional work will be done to revise the software to permit masking of spectral regions influence by interferences, as is done in an FTIR. This may yield an even lower interference response, especially for NH₃.

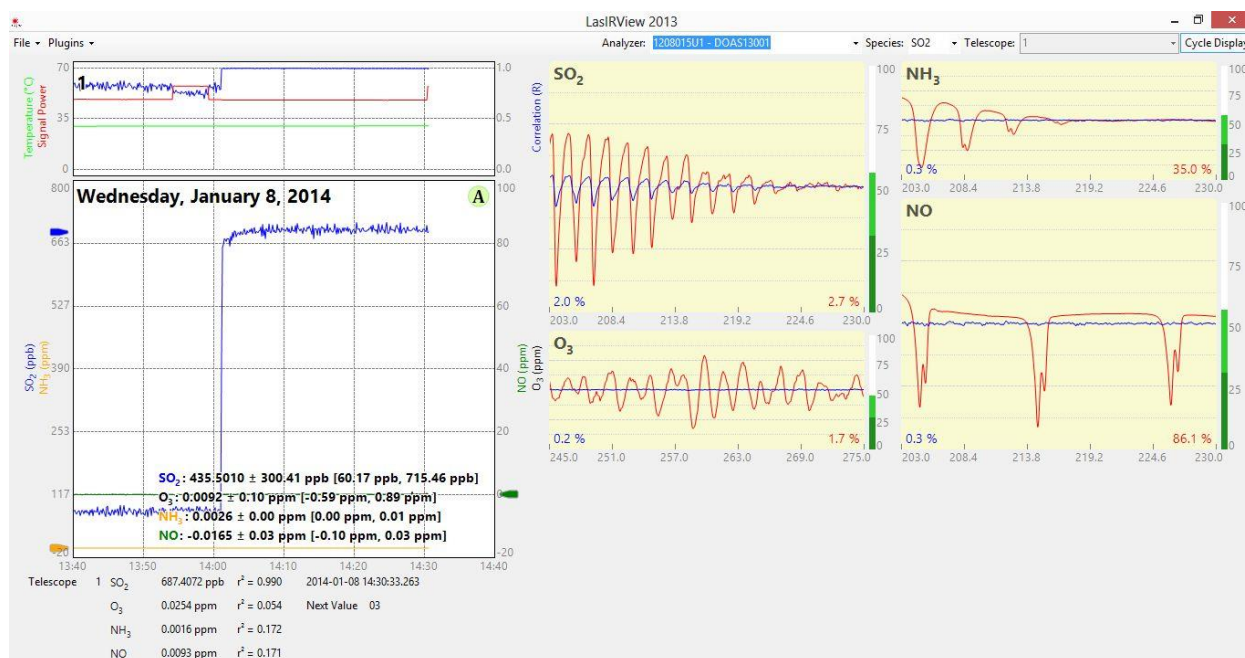


Figure 5-13. Shows DOAS SO₂ 5-second response at 680 ppbV using the original configuration file and spectral range of analysis between 203 and 230 nm. All linearity tests were done with this spectral range of analysis.

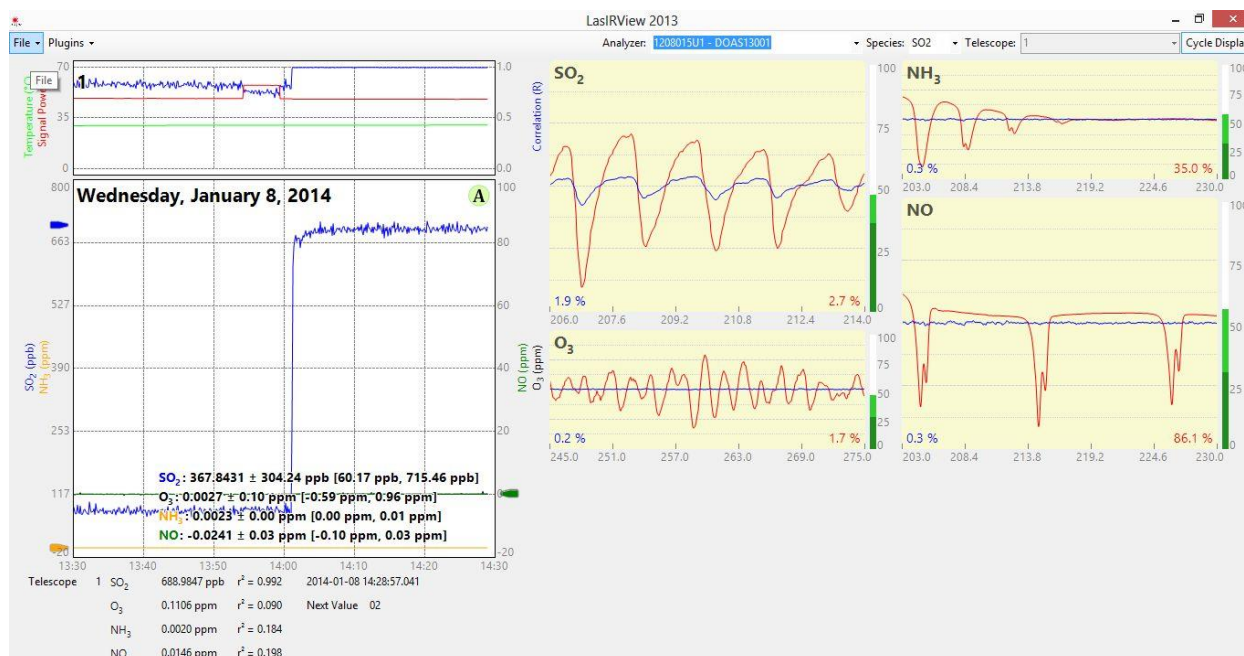


Figure 5-14. Shows DOAS SO₂ 5-second response at 680 ppbV, using the new configuration file and spectral range of analysis between 206 and 214 nm. The response is similar at this narrower spectral range, which is where the primary SO₂ absorptions take place.

To test for potential interferences with formaldehyde, a permeation tube was used. The permeation tube provides high concentrations of formaldehyde, which are well above those that would be found in typical vehicle exhaust. Thus, this represents an extreme upper limit of interference that might be seen in an actual application. For the present tests, sampling from the permeation tube did show any impacts on the spectral lineshape or SO₂ concentration. Thus, it is concluded that formaldehyde would not be an interferent for the SO₂ measurement for this DOAS.

5.4 Vehicle Emission Tests

Vehicle emissions measurements were conducted in CE-CERT's Vehicle Emissions Research Laboratory (VERL). The centerpiece of the VERL is a 48-inch Burke E. Porter single-roll electric chassis dynamometer, capable of testing vehicles weighing up to 12,000 lbs. A Pierburg Positive Displacement Pump-Constant Volume Sampling (PDP-CVS) system is in conjunction with a Pierburg/AVL AMA-4000 emissions bench for emissions measurements.

Several vehicles were tested in this portion of the program, including a 2012 Nissan Versa, a 2013 VW Jetta GLI, and a 2013 Dodge Ram 2500 diesel pickup truck. The primary purpose of the vehicle exhaust measurements was to evaluate if any additional interfering species needed to be accounted for, outside of those used in the calibration gas verification tests. Overall, the results were consistent with the results from the calibration gas tests. In general, for the vehicles without NH₃, there did not appear to be any significant interferences to the SO₂ measurements. On the other hand, vehicles for which NH₃ was found in the exhaust at levels above 11 ppm, did show a significant interference.

The best performance for the DOAS was on 2012 Dodge Ram diesel pickup truck. The DOAS results for the diesel Dodge Ram are provided below. Figure 5-15 shows the DOAS output after the diesel vehicle is turned on. The results show a significant amount of NO, greater than 50 ppmV, but

very little SO₂ (-1.105 ppbV) and NH₃ (.025 ppmV). These results show that NO does not bias the SO₂ at these levels over the fit limits chosen (209 to 213 nm), so NO is not an interferent. The SO₂ levels are very low, and the SO₂ measurement is at the expected detection limits. Figure 5-16 shows that as the test progresses, the NO level decreases, while the SO₂ initially remains at/below the detection limit. Finally, near the latter stages of the test as shown in Figure 5-17, SO₂ is measured above the detection limit, at a level of approximately 26 ppbV. Clearly, in a low NH₃ environment, as tested here the SO₂ detection is unbiased and meets the laboratory tested detection limits of around 20 ppbV. If the DOAS is used in a low NH₃ environment, as in this test, it should achieve the expected detection limits.

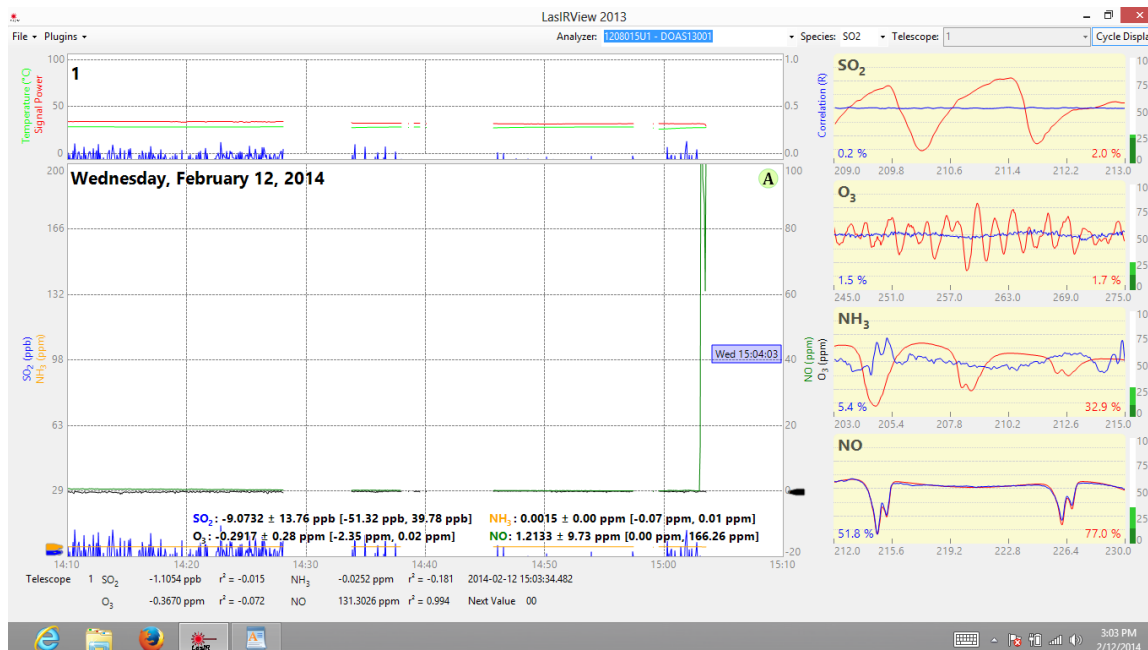


Figure 5-15: Diesel test at engine turn on, note there is no detectable SO₂ (-1.105 ppbV).

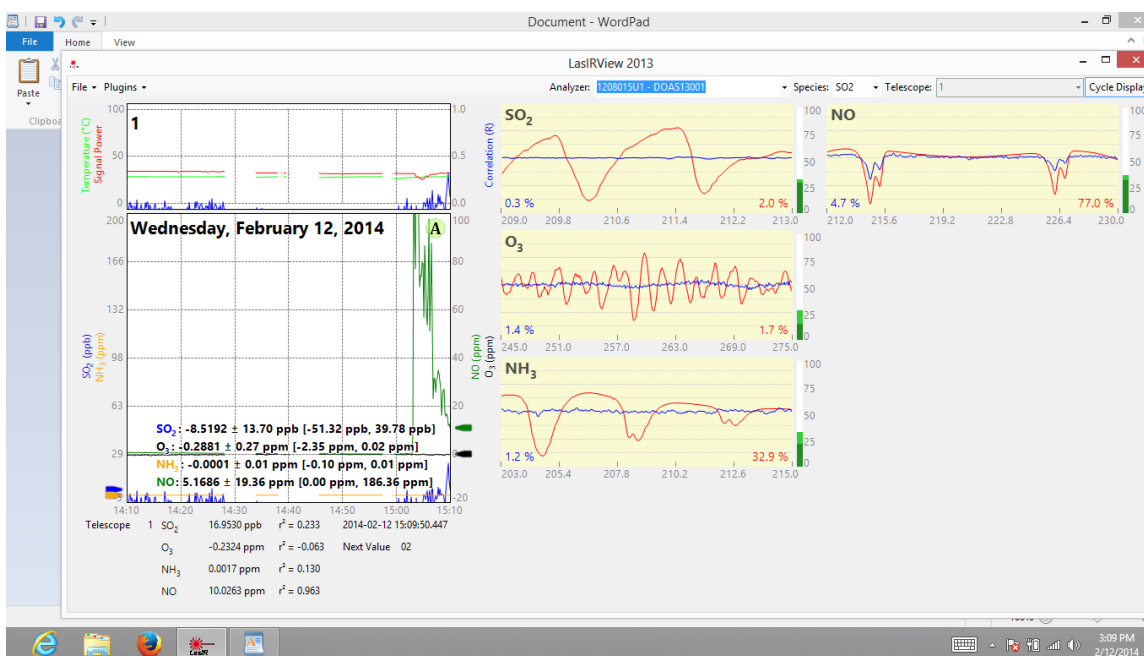


Figure 5-16: progression of diesel test still SO₂ measured below detection limit



Figure 5-17: Progression of diesel test with SO₂ now measured above the detection limit.

The gasoline vehicles, on the other hand, showed higher levels of NH₃, and as such showed periods where a significant negative bias was found. The 2012 Nissan Versa emitted up to 100 ppm or more of NH₃ during various parts of the cycle. The laboratory tests showed that once the levels exceeded 11.0 ppmV of NH₃, there became a statistically significant negative bias to the SO₂ response.

Figure 5-18 shows the DOAS spectral response for the three species measured, NO, NH₃ and SO₂. As can be seen, that the raw NH₃ spectrum over the range measured (203-215 nm) from the vehicle (blue) lies virtually on top of the reference NH₃ spectrum (red). At this point in the test, the NH₃ being measured from the vehicle is 22.798 ppmV. Concurrently looking at the SO₂ spectrum over the same range measured (209-213 nm), an overall negative bias caused by the NH₃ interference, which results in measured SO₂ values of – 38.898 ppbV.

This trend is shown in the overall test run, as shown in Figure 5-19, where once the values exceed 11 ppmV of NH₃, the SO₂ measured values go negative. This interference is also non-linear as once the NH₃ values approach 80 ppmV, the SO₂ measured values are greater than -900 ppbV.

The DOAS is designed to measure SO₂ out of diesel engines where NH₃ levels are typically less than 10 ppmV. If it is to be used for vehicles with higher levels of NH₃, an NH₃ scrubber would likely be needed to scrub the level of NH₃ in the exhaust to no greater than 10 ppmV, as well as perhaps some additional updates to the software that are currently being developed.

It should be noted that in addition to the capability of measuring SO₂ in the exhaust, as per the original program scope, this DOAS also has the capability of measuring NH₃ in real-time. For the Nissan Versa, a tunable diode laser system (TDLAS) that was designed to measure NH₃ in raw vehicle exhaust was run concurrently with the DOAS. Figure 5-20 shows the measured results from the DOAS and the TDLAS. The results show a good correlation between the TDLAS results and the DOAS results for NH₃, at NH₃ levels below 90 ppm. A regression plot (Figure 5-21) shows a high correlation between the two measurements, with an $R^2 = .951$, but once the NH₃ levels exceed 90 ppm the DOAS UV light source is too attenuated to make a measurement. Also, looking at the regression plots, it can be seen that the DOAS is reading slightly lower than the TDLAS at higher levels, likely from saturation of the UV spectra.

Figure 5-22 shows the DOAS response under conditions where NH_3 levels were much lower, in this case 1.486 ppmV. Here, the SO_2 is measured at 8.997 ppbV, and does not show any negative bias in the measured spectra. At these lower NH_3 levels the DOAS appears to meet the objectives of better than 20 ppbV detection limits.

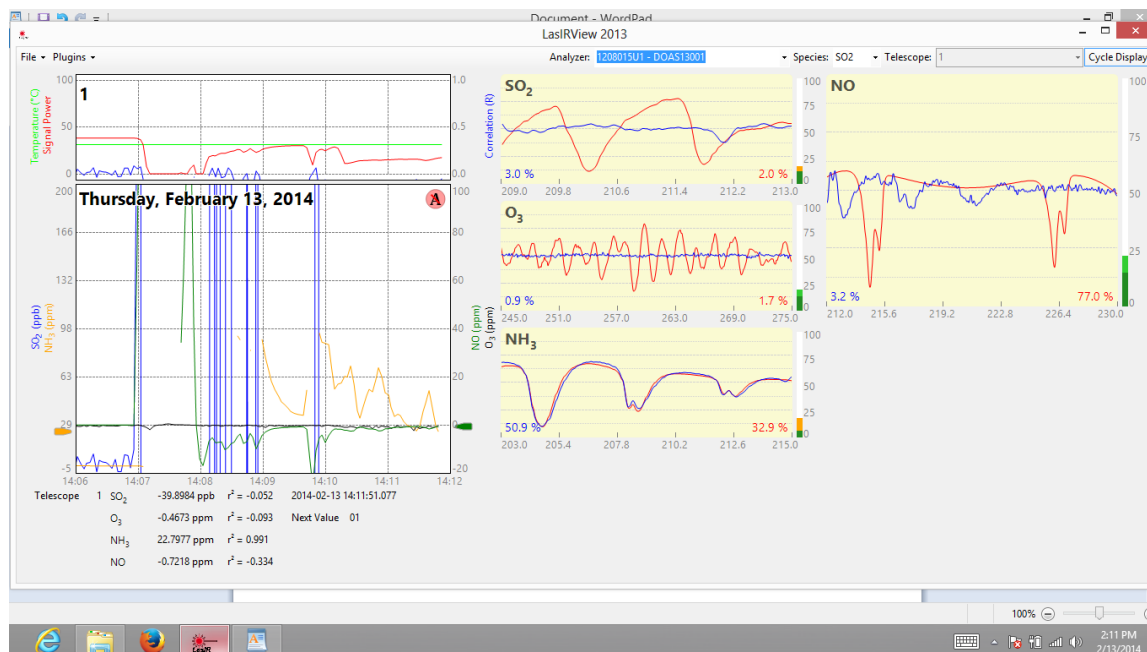


Figure 5-18. DOAS spectral response under high NH_3 conditions showing a negative bias to SO_2 measured values.

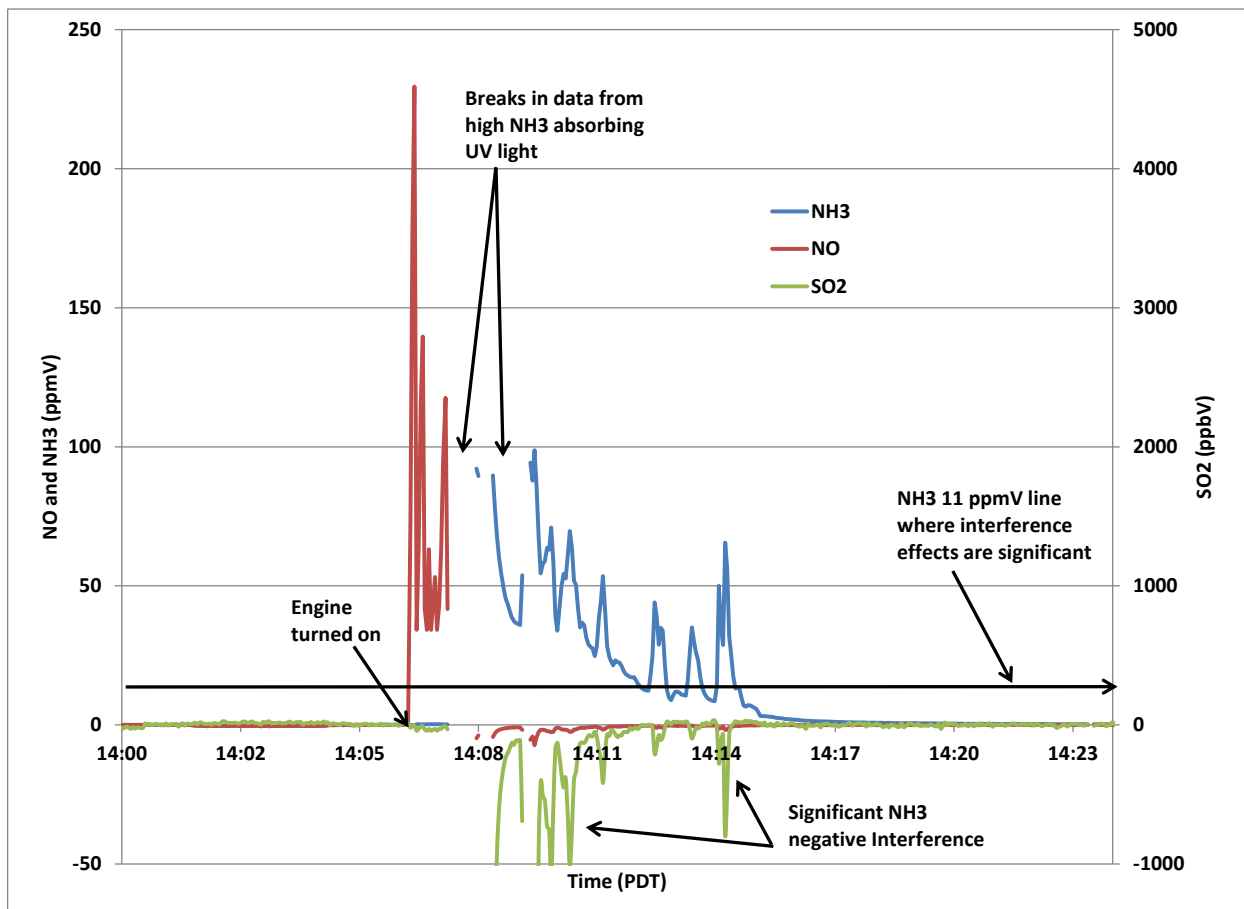


Figure 5-19. DOAS measured values for the 2012 Nissan Versa emissions test. Note the drop off of the signal once NH_3 levels reached 90 ppmV, and the significant negative bias to SO_2 under these high NH_3 conditions.

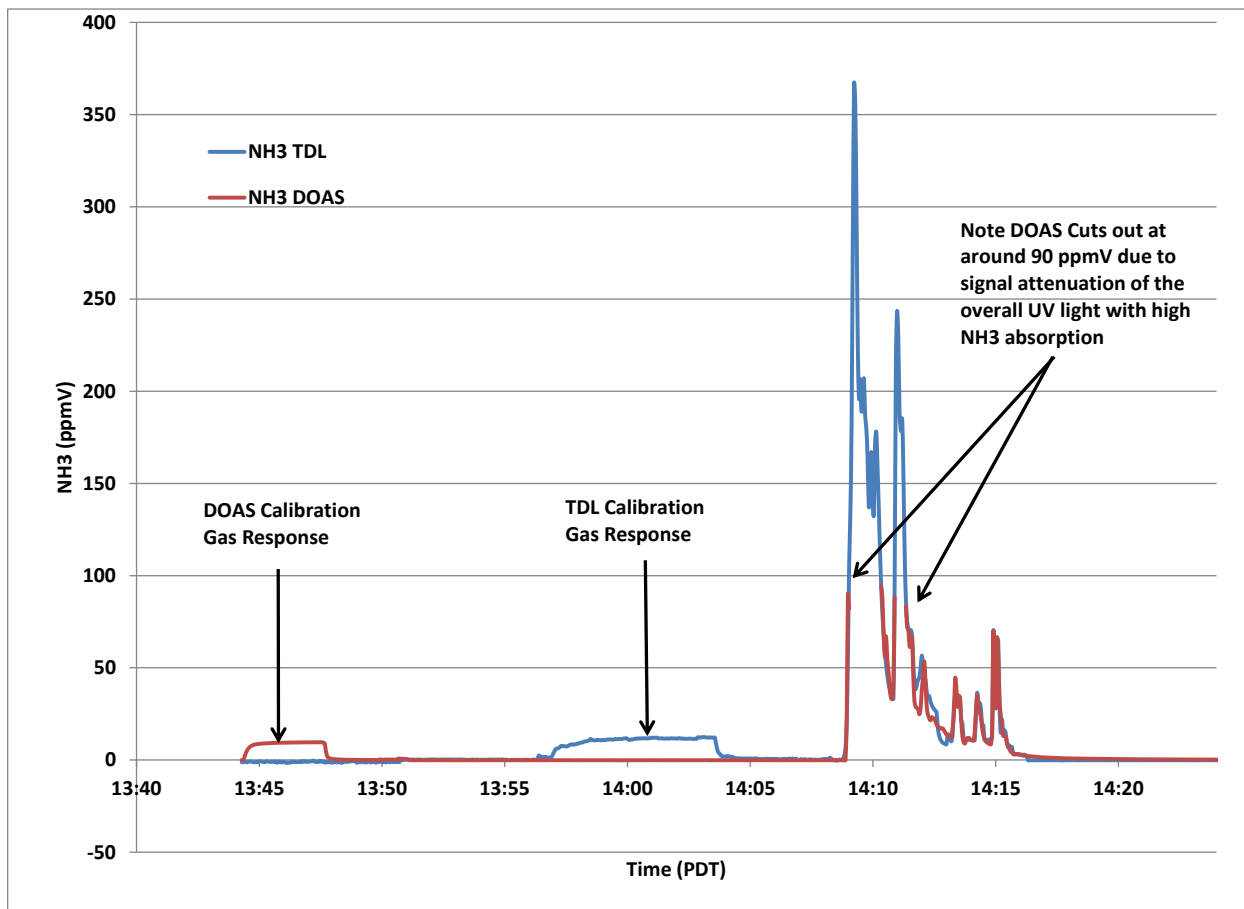


Figure 5-20. NH₃ emissions measurements for the DOAS along with concurrent measurements with a tunable diode laser system configured for NH₃ for the 2012 Nissan Versa. Both are raw exhaust measurements. Note the high similarity in response between the two separate and distinct spectral techniques.

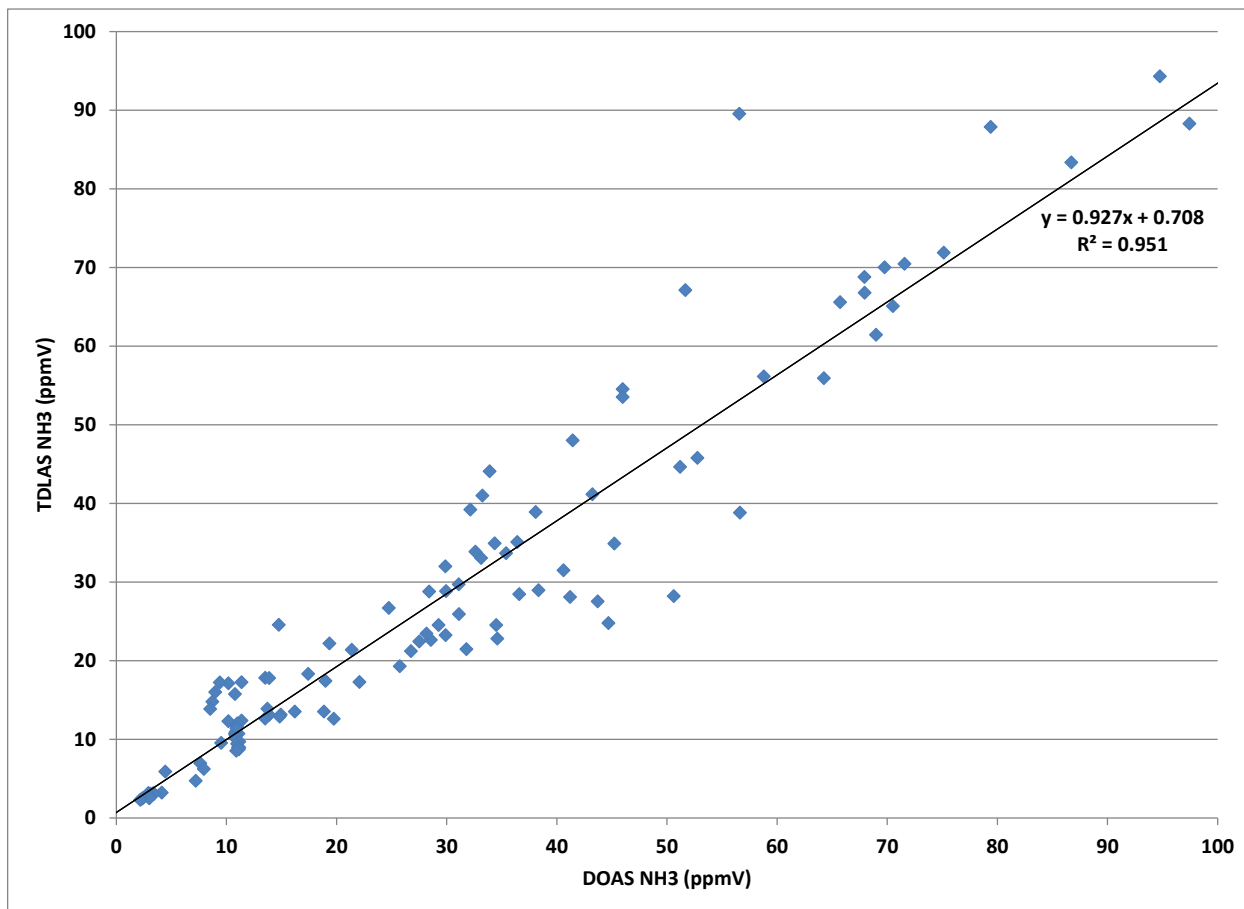


Figure 5-21. Regression plot NH₃ emissions for the 2012 Nissan Versa for the DOAS compared with an NH₃ tunable diode laser system. Both are raw exhaust measurements. Note the high correlation between the two techniques for values up to 90 ppmV with an R² of 0.951.

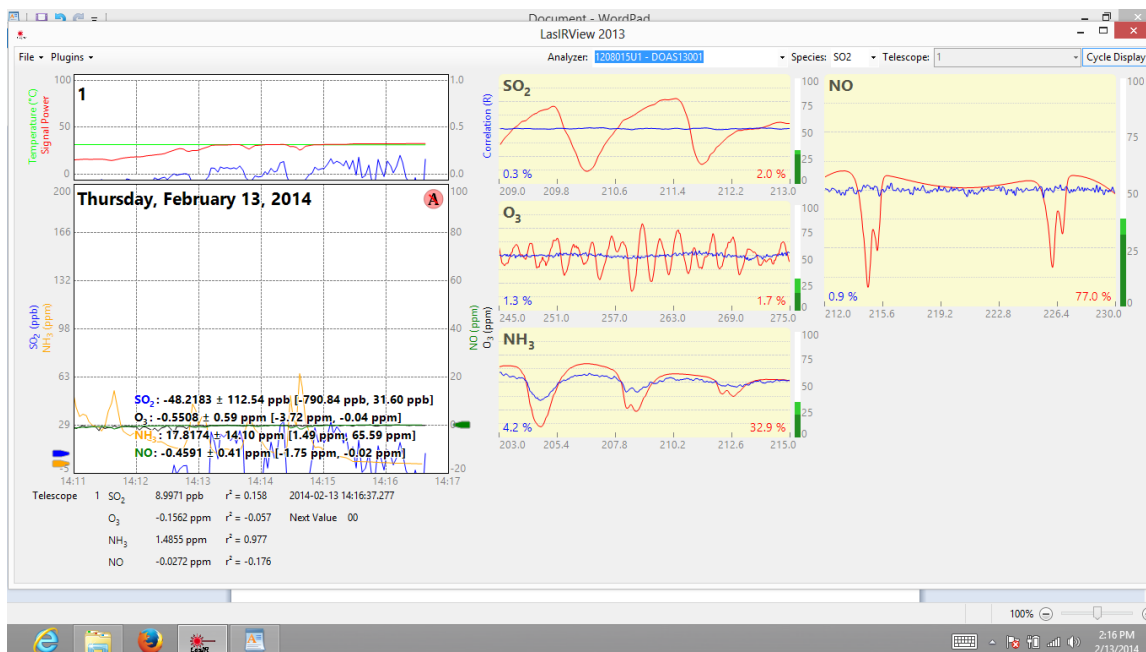


Figure 5-22. DOAS Spectral response under low NH₃ conditions, typical to diesel engines, the spectral response and the calculated numbers for SO₂ show no negative bias.

6 Installation/Verification at CARB Facility

Once the instrument is completed and tested at UC Riverside, it will be taken to, and installed at, one of CARB's laboratories. Installation will include verification and on-site calibration of the instrument, training, and an evaluation of the system on one test vehicle, which will be provided by CARB. The on-site installation, verification, and training for the DOAS is expected to take one week or less.

The installation of the DOAS will be done in coordination with CARB staff from the laboratory where it will be installed. UC Riverside will provide a description and size measurements for all components of the DOAS system to CARB laboratory staff prior to the installation period, and will work with CARB staff to identify a suitable location for the instrument and all associated equipment. UC Riverside will also participate in meetings, as needed, to ensure the laboratory is ready for installation, both phone call/conference call meetings and site visits.

CARB will be responsible for providing a sample delivery system (from the location where sampling is done to the instrument itself) and any fabrication required for installation of the instrument in the laboratory. The sample delivery system should include a sample pump, heated lines, and a heated filter to reduce PM contamination. CE-CERT will discuss sampling requirements/parameters with CARB staff prior to the purchase of these items to ensure they meet the requirements for the instrument. Once the instrument is ready for installation, and the laboratory has completed preparations for installation, UC Riverside will bring the instrument to the CARB laboratory and set it up. Initial set-up of the instrument in the laboratory is expected to take 1 to 2 days.

Once the instrument set-up is complete, instrument operation and accuracy will be verified with calibration gas. The calibration/verification of the DOAS will be done using calibration gases in a range similar to concentration levels expected in raw exhaust; this range will be the same as that used for calibration of the instrument in the bench laboratory tests. The instrument calibration curve will consist of several points spanning the desired concentration range. The detection limits of the instruments will be established based on one standard deviation of the noise in the time resolved data under conditions where the instrument is zeroed and at several calibration points.

Following calibration/verification of the DOAS, UC Riverside will train CARB laboratory staff on the operation of the instruments. Training will occur on both the software and hardware components of the system, the general principles of instrument operation, and a discussion of any elements of the instrument that may require routine maintenance/repair. Training is expected to take approximately one day. A manual will also be provided to CARB staff, either at the time of installation or at some subsequent point, and will provide a description of the unit, a description of the scientific principles of the instrument's operation, instructions on how the instrument is operated, and a description of any parts needed for routine maintenance. A software manual will be provided by Unisearch and will be included in the system manual.

Overall, instrument installation, set-up, verification, calibration, and training can be completed in the period of approximately one week or less. This would include testing on actual vehicle exhaust from vehicles provided by CARB (and with fuels provided by CARB). Initial testing will focus on measurements in raw exhaust. Sulfur in the fuel and oil will provide baseline SO₂ measurements for vehicle testing. SO₂ levels in the exhaust can also be varied to look at a wider range of SO₂ concentrations, if needed. This could include direct injection of SO₂ calibration gas into the exhaust stream.

7 Summary and Conclusions

Understanding the nature of the sulfur and sulfate in combustion and lubricant-derived particles is important to characterize to better understand the relative contribution of fuel vs. oil sulfur, to understand storage vs release of sulfur from catalyzed surfaces, and measure the sulfur fraction partitioning into the PM nucleation particles. The objective of this research is to construct, test and provide to ARB laboratories a differential optical absorption spectrometer (DOAS) that can measure down to 20 ppbV in real time and determine a mass balance between SO₂ and sulfate. The DOAS developed under this program was evaluated using a series of laboratory performance tests at the CE-CERT laboratory. The DOAS will be installed and operated in the ARB Heavy Duty Emissions Test Laboratory. The major conclusions from the findings are summarized in the following:

- The differential optical absorption spectrometer (DOAS) developed for this project was specially designed and built for rapid, extractive detection of sulfur dioxide at low ppb levels for the ARB. The integrated system consists of the extractive sampling train, the sampling cell, and the spectrometer.
- The sample cell uses a single-path design with beam expanding and focusing optics to minimize cell volume. The sample cell designed as an open cell with the sample cell residing between the windows, rather than having the transmitting and collecting optics inside the sample cell.
- The sample cell for this system is cylindrical with a length of 1.0 m. The total volume of the DOAS sample cell is approximately 0.51 liters.
- The cell is designed to operate over a full 8-10 hour testing day at a temperature of 110°C, with a temperature range from 25°C up to 120°C (250°F).
- To avoid possible interferences from other exhaust constituents, the spectral range was restricted to the UVB region (200–230 nanometer (nm)). For the 200–230 nanometer (nm) region, a deuterium lamp was used as the light source. Some additional adjustments were also made to the DOAS to narrow the spectral range to 206 nm to 214 nm, to compensate for an NH₃ interferent.
- The spectrometer/receiver consists of a single working element, a concave 1200 groove/millimeter (mm) holographic diffraction grating optimized for 200–230 nm.
- The DOAS software, LasIRView 2009, is a user-friendly Windows-based based package with outputs for data logging and a software manual.
- Laboratory tests were conducted to evaluate the response of the SO₂ monitor to a range of operating conditions, from ambient conditions to those most representative of exhaust gas emanating from vehicles.
- Detection limits were approximately in the range of 12 to 15 ppbV at three times the standard deviation of zero gas response.
- The linearity of the instrument was evaluated over SO₂ concentration ranges of 20 to 192 ppbV and 51 to 953 ppbV. The regression analysis showed a slope of 1.011 and 0.995, respectively, and R² values of 1.0 and 0.999, respectively, for these ranges.

- A number of interference tests were conducted, focusing on potential interferences between SO₂, NO, and NH₃. SO₂ was not found to interfere with either NO or NH₃, at levels of 80 ppbV and 680 ppbV. Initial tests at 300 ppmV of NO and 16.6 ppmV of NH₃ confirmed that at these high levels they would interfere with the SO₂ response over the spectral range specified. To mitigate the impact of these interferences, the spectral range was modified to focus on a narrower range of 206 to 214 nm. With the new spectral range of analysis, the DOAS interference SO₂ response was less than 1.5 ppbV with 300 ppmV of NO injected with, and was slight less than 8 ppbV with 16.6 ppmV of NH₃ injected.
- The DOAS was evaluated over vehicle emissions tests in CE-CERT's light-duty chassis dynamometer laboratory. A 2012 Nissan Versa, a 2013 VW Jetta GLI, and a 2013 Dodge Ram 2500 diesel pickup truck were tested. The results showed no appreciable SO₂ interferences for the tests on the diesel truck, which had very low NH₃ emissions. Clearly, in a low NH₃ environment, as tested here the SO₂ detection is unbiased and meets the laboratory tested detection limits of around 20 ppbV. If the DOAS is used in a low NH₃ environment, as in this test, it should achieve the expected detection limits.
- The gasoline vehicles, on the other, had higher levels of NH₃, and showed a significant interference. Essentially, when the NH₃ values exceeded 11 ppmV, the SO₂ measured values go negative. This interference is also non-linear as once the NH₃ values approach 80 ppmV, the SO₂ measured values are greater than -900 ppbV. If it is to be used for vehicles with higher levels of NH₃, an NH₃ scrubber would likely be needed to scrub the level of NH₃ in the exhaust to no greater than 10 ppmV, as well as perhaps some additional updates to the software that are currently being developed.
- This DOAS also has the capability of measuring NH₃ in real-time. Comparisons were made between the DOAS and an NH₃ tunable diode laser. The results showed a good correlation between the TDL and DOAS results for NH₃, at NH₃ levels below 90 ppmV, with a regression coefficient of $R^2 = .951$, but once the NH₃ levels exceed 90 ppmV the DOAS UV light source is too attenuated to make a measurement.

Recommendations for Future Work

Based on the results of this study, several recommendations for future work can be provided. This includes recommendations for further development of the instrument, as well as recommendations based on the laboratory testing that was conducted. For the DOAS itself, the initial work report here suggests that this instrument could be further developed/optimized to provide concurrent measurements of NO and NH₃. To expand the measurement capability for the NH₃, some additional development work would be needed to address the fact that the DOAS UV light source is too attenuated to make a measurement once the NH₃ levels exceed 90 ppm. The possibility of expanding the DOAS for use in other applications or for other species is also potentially of value. Another interesting finding from the laboratory tests was the higher than expected NH₃ emissions for some of the test vehicles. In particular, both of the gasoline vehicles tested for this study produced higher than expected NH₃ emissions, even though both vehicles represented late model vehicle technologies. While these vehicles were tested under a very narrow range of conditions, these initial results suggest that further investigation over a wider range of vehicles and conditions to see how prevalent the higher NH₃ emissions levels might be and if this could be an important issue with respect to tailpipe emissions.

References

1. Williamson W B SHK and GH. Poisoning of Platinum–rhodium Automotive Three-way Catalysts: Behavior of Single-component Catalysts and Effects of Sulfur and Phosphorus. *Environmental Science and Technology*. 1980;14:319–24.
2. Williamson WB, Gandhi HS, Heyde ME, Zawacki GA. Deactivation of Three-way Catalysts by Fuel Contaminants: Lead, Phosphorus, and Sulfur. SAE Technical Paper. 1979;790942.
3. Yao H C SHK and GHS. The Effects of SO₂ on the Oxidation of Hydrocarbons and Carbon Monoxide over Pt/Al₂O₃ Catalysts. *Journal of Catalysis*. 1981;67:231–6.
4. Yao YF, Yu J. The Oxidation of Hydrocarbons and CO over Metal Oxides. *Journal of Catalysis*. 1975;26:266–75.
5. Alliance of Automobile Manufacturers (AAM) and the Association of International Automobile Manufacturers (AIAM). Industry Low-Sulfur Test Program. Presented to the California Air Resources Board. 2001.
6. American Automobile Manufacturers Association (AAMA) and the Association of International Automobile Manufacturers (AIAM). Study on the Effects of Fuel Sulfur on Low Emission Vehicle Criteria Pollutants. 1997.
7. Schleyer CH, Gorse RA, Gunst RF, Barnes GJ, Eckstrom J, Eng KD, et al. Effect of Fuel Sulfur on Emissions in California Low Emission Vehicles. SAE Technical Paper. 1998;1998–10–19.
8. Koehl WJ, Benson JD, Burns VR, Gorse RA, Hochhauser AM, Knepper JC, et al. Effects of Gasoline Sulfur Level on Exhaust Mass and Speciated Emissions: The Question of Linearity - Auto/Oil Air Quality Improvement Program. SAE Technical Paper. 1993;1993–10–01.
9. Leppard WR, Koehl WJ, Benson JD, Burns VR, Hochhauser AM, Knepper JC, et al. Effects of Gasoline Properties (T50, T90, and Sulfur) on Exhaust Hydrocarbon Emissions of Current and Future Vehicles: Speciation Analysis - The Auto/Oil Air Quality Improvement. SAE Technical Paper. 1995;1995–10–01.
10. Leppard WR, Koehl WJ, Benson JD, Burns VR, Hochhauser AM, Knepper JC, et al. Effects of Gasoline Properties (T50, T90, and Sulfur) on Exhaust Hydrocarbon Emissions of Current and Future Vehicles: Modal Analysis - The Auto/Oil Air Quality. SAE Technical Paper. 1995;1995–10–01.
11. Rutherford, J.A., Burns, V.R., Leppard, W.R., Rippon, B.H., Koehl, W.J., Hochhauser, A.M., Painter, L.J., Reuter, R.M., Benson, J.D., Knepper, J.C., and Rapp LA. Effects of Gasoline Properties on Emissions of Current and Future Vehicles –T50, T90, and Sulfur– The Auto/Oil Air Quality Improvement Research Program. SAE Technical Paper. 1995;(952510).
12. Benson JD, Burns V, Gorse RA, Hochhauser AM, Koehl WJ, Painter LJ, et al. Effects of Gasoline Sulfur Level on Mass Exhaust Emissions – Auto/Oil Air Quality Improvement Research Program. SAE Technical Paper. 1991;(912323).

13. Truex TJ. Potential for Improved Sulfur Tolerance in Three-way Automotive Catalysts. Final Report Prepared for the American Petroleum Institute; 1997.
14. Diesel Emission Control – Sulfur Effects (DECSE) Program. Phase I Interim Data Report No. 1; 1999.
15. Advanced Petroleum-based Fuels - Diesel Emissions Control Project (APBF-DEC) - Lubricants Project Phase 1. Summary; 2004.
16. Advanced Petroleum-based Fuels - Diesel Emissions Control Project (APBF-DEC) - Lubricants Project Phase 2. Final Report; 2006.
17. Diesel Emissions Control- Sulfur Effects Project (DECSE). Produced for the U.S. Department of Energy (DOE) by the National Renewable Energy Laboratory (NREL), a DOE national laboratory; 2002.
18. Ingalls M, Springer K. Measurement of Sulfate and Sulfur Dioxide in Automotive Exhaust. SWRI Final Report; 1976.
19. Graham L. Gaseous and Particulate Matter Emissions from In-use Light-duty Gasoline Motor Vehicles. Report No 99-67 Environment Canada, Ottawa, Ontario, Canada; 1999.
20. Chow J C, Watson J G, Bowen J L, Frazier C A GAW, Fung K K LD and AL. A sampling System for Reactive Species in the Western US Sampling and Analysis of Airborne Pollutants ed E D Wine. 1993;209–28.
21. Watson J C, Chow J C, Lowenthal D H PLC and, A FC. Differences in the Carbon Composition of Source Profiles for Diesel- and Gasoline-powered Vehicles. Atmospheric Environment. 28:2493–505.
22. Pisano JT, Sauer C, Robbins J, Miller JW, Gamble H, Durbin TD. A UV Differential Optical Absorption Spectrometer for the Measurement of Sulfur Dioxide Emissions from Vehicles. MEASUREMENT SCIENCE AND TECHNOLOGY. 2003;14:2089–95.

